

# Application of the ChlorOut concept in a Waste Wood fired CFB Boiler

Mårten Carlberg



## Abstract

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Boilers converting from sulphur rich fossil fuels to alkali and chlorine rich bio fuels often experience an increased super heater corrosion. This is partly due to the increased formation of KCl during combustion of bio fuels. The problem could, for instance, be handled with a sulphur containing additive to the fuel or to the flue gases. This diploma work was carried out at Vattenfall Power Consultant AB and it focuses on the so-called ChlorOut concept. The ChlorOut concept has been developed by Vattenfall to minimise deposit formation and corrosion. It consists of IACM, an instrument for on-line measurements of gaseous alkali chlorides, and a sulphate-containing additive that converts alkali chlorides to less corrosive alkali sulphates. The sulphate-containing additive is often ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ . The main objective was to evaluate a ChlorOut installation in a CFB (Circulating Fluidised Bed) boiler in Germany. This boiler burns waste wood and has experienced super heater corrosion problems. IACM measurements showed very high levels of alkali chlorides in the flue gas. Results showed that adding  $(\text{NH}_4)_2\text{SO}_4$  reduced KCl measured by IACM and also the chlorine content in deposits in the super heater region. The deposits was collected by using temperature controlled steel rings on a deposit probe. The fast response for KCl from IACM enables controlling the flow of  $(\text{NH}_4)_2\text{SO}_4$  when fuel quality varies. The results indicated a reduction of the chlorine induced corrosion in the boiler when using the ChlorOut concept.

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## Sammanfattning

Det ökande intresset för miljöfrågor genomsyrar idag debatten om hur vår framtida energiförsörjning skall se ut. Länderna inom den europeiska unionen (EU) har enats om att den totala energitillförseln inom EU år 2020 skall bestå av 20 % förnyelsebara energikällor. För att möta detta mål har exempelvis olika styrmedel införts vilka gör det fördelaktigt för energiproducenter att ställa om sin produktion. Resultatet har blivit att mer och mer vindkraft byggs samt en ökning i konverteringen från fossilbränslen till koldioxidneutrala biobränslen i förbränningsanläggningar.

Det ökande användandet av biobränslen har gett upphov till nya problem som måste lösas. Biobränslen kräver nya brännare, och en mer varierande bränslekvalitet kräver mer aktiv styrning av förbränningsprocessen. Ett annat problem som uppstått är en ökning av korrosionen på överhettartuber och pannväggar med negativa ekonomiska konsekvenser som resultat. En av anledningarna till korrosionsökningen är biobränslenas höga halter av alkalimetaller (Na (natrium), K (kalium)) och klor (Cl) som under förbränning bildar alkaliklorider (KCl (kaliumklorid), NaCl (natriumklorid)). Alkaliklorider är oftast i gasfas när de når området med överhettartuberna i förbränningsanläggningar men kondenserar ut i smält fas på de kallare tuberna. En ökad korrosion på grund av en ökad halt klorid på överhettartuber från biobränsleeldade pannor har kunnat påvisas i [1] och [2].

Problemet hanteras idag i huvudsak genom samförbränning av biobränslen och ett fossilt bränsle som torv eller genom tillsats av ett additiv. Additivet kan tillsättas till bädden eller till rökgaserna och innehåller svavel. Svavel är effektivt eftersom det kan binda alkaliklorider till alkalisulfater ( $K_2SO_4$ ,  $Na_2SO_4$ ) som har högre smältpunkt än kloriderna och kondenserar därför till partiklar i rökgasen innan de når överhettarna. Både samförbränning [3] och tillsats av ett additiv till rökgaserna [4], [5] har visat sig effektivt för reduktionen av alkaliklorider.

Vattenfall Power Consultant AB reducerar idag alkaliklorider, inom konceptet ChlorOut, genom tillsats av additiv till rökgaserna. ChlorOut består av ett instrument, IACM (In situ Alkali Chloride Monitor) som kontinuerligt mäter mängden alkaliklorid och svaveldioxid ( $SO_2$ ) i rökgaser samt ett additiv (oftast ammoniumsulfat,  $(NH_4)_2SO_4$ ) som sprayas på rökgaserna innan överhettarna vid temperaturer under  $1000^\circ C$  (SNCR, Selective Non Catalytic Reduction, området). KCl halten som mäts av instrumentet används till att styra mängden sulfat som doseras till rökgaserna. I olika mätkampanjer har ammoniumsulfat visat sig reducera mängden klorid i beläggningar på överhettartuber bättre än vad samförbränning gjort [6], [7]. En extra effekt när man tillsätter ammoniak i SNCR området är reduktion av  $NO_x$  (kväveoxider). CO (kolmonoxid) tenderar också att påverkas vid tillsats av ammoniumsulfat.

I detta examensarbete har en ChlorOut installation utvärderats i en CFB (Circulating Fluidized Bed) panna i Bergkamen, Tyskland. Pannan bränner RT-flis (Retur Trä flis) och IACM mätningarna visar ovanligt höga halter av alkaliklorider i rökgaserna. Inom arbetet har olika doseringspunkter för ammoniumsulfaten utvärderats för att bästa effekt av sulfaten skall uppnås.

Mätningar som utförts är beläggningmätningar med en beläggningssond samt kontinuerliga IACM mätningar. Data från anläggningens egen mätutrustning har också använts. Analyser av beläggningar utfördes med ett SEM/EDX mikroskop (Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis).

Resultaten från analyserna visar att det är möjligt att mäta andelen alkaliklorider i rökgasen med IACM instrumentet. Resultaten visar även att en tillsats av ammoniumsulfat till rökgasen i Bergkamen reducerar andelen alkaliklorider i rökgasen. Samtidiga beläggningmätningar visar att andelen klor i beläggningarna minskar vid dosering av sulfat i jämförelse med då ingen dosering utfördes. Resultaten visar även att ett ökat flöde av ammoniumsulfat ökar sulfateringen av alkaliklorider i rökgasen och minskar andelen klor i beläggningarna.

Ett användbart mått för bestämning av korrosionsrisken hos ett bränsle har varit kvoten S/Cl. Detta mått är pålitligt men tar tid att få fram. Inom detta arbete har kvoten SO<sub>2</sub>/KCl, mätt med IACM, tagits fram och jämförts med kloridinnehållet i beläggningarna mätta med beläggningssonden. Resultaten visar att on-line svaren från IACM instrumentet kan användas för att förutse korrosionsrisken i en förbränningsanläggning. Kvoten kan även vara lämplig för styrningen av ammoniumsulfatflödet in i pannan.

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# 1 List of abbreviations

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Ammonium sulphate
C	Carbon
Ca	Calcium
CFB	Circulating Fluidised Bed
Cl	Chlorine
CO	Carbon monoxide
EU	European Union
FBC	Fluidised Bed Combustion
FexO <sub>x</sub>	Ferric oxides
H <sub>2</sub> S	Hydrogen sulfide
HCl	Hydrogen chloride
HO <sub>2</sub>	Hydroperoxyl, Perhydroxyl
IACM	In situ Alkali Chloride Monitor
INTREX	Type of super heater located in the loop seal
K	Potassium
KCl	Potassium chloride
KOH	Potassium hydroxide
Mg	Magnesium
MWel	Electrical effect
MWth	Thermal effect
Na	Sodium
NaCl	Sodium chloride
NH <sub>3</sub>	Ammonia
NO <sub>x</sub>	Nitrogen oxide
O <sub>2</sub>	Oxygen
OH	Hydroxide
PID-regulator	Proportional Integrating Derivation- regulator
R#	Reaction number (#= 1, 2, 3 . . . )
RT-flis	Flis från returträ (Swedish for waste wood)
S	Sulphur
SCR	Selective Catalytic Reduction
SEM/EDX	Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis
SH#	Super Heater (#=1, 2)
Si	Silica
SNCR	Selective Non Catalytic Reduction
SO <sub>2</sub>	Sulphur dioxide
SO <sub>3</sub>	Sulphur trioxide
T#	Test number (#=1, 2, 3, ...)
TP#	Test Period (#=1, 2)

## 2 Introduction

The growing interest for environmental questions permeates today the debate of how our future energy systems will look like. A goal for the year 2020 was set by the European Union that 20 % of the unions total energy production should come from renewable energy sources. An effect of the goal is, for example, an increase in wind power production and increased conversion from fossil fuels to CO<sub>2</sub> (carbon dioxide) neutral biofuels during combustion for energy production.

The increased use of biofuels can lower the CO<sub>2</sub> to the atmosphere but it has also given birth to new problems that have to be handled. A more active control of the combustion due to varying quality of biofuels, new burners and increased corrosion are a few problems encountered in the adaptation to the new goals. Increased corrosion has economical concerns as it often implies a more frequent change of the super heaters. The cause for the increased corrosion is mainly the high alkali content in the biofuels that during combustion forms alkali chlorides (KCl (potassium chloride), NaCl (sodium chloride)). These alkali chlorides have a low melting point and can easily condense as chloride melts on cold surfaces in the boiler. Increased chlorine induced corrosion has been observed in several boilers when burning biofuels with high alkali and chloride contents like waste wood, straw and forest residues [1], [2].

The increased corrosion is today, in general, handled by co-burning the bio fuel with sulphur granulates or with a sulphur rich fuel such as peat or coal. Another solution is adding a sulphur-containing additive to the flue gas. Both co-combustion of peat [3] and adding a sulphur-containing additive to the flue gas [4], [5] have shown effective in the reduction of alkali chlorides condensed on super heaters. Sulphur is effective as it can form alkali sulphates (K<sub>2</sub>SO<sub>4</sub> (potassium sulphate), Na<sub>2</sub>SO<sub>4</sub> (sodium sulphate)) from sulphation of alkali chlorides in the flue gas or from direct formation of alkali sulphates during combustion. The sulphates have higher melting point than the chlorides and condense to particles in the flue gas before they hit the super heaters. Silicates and earth alkalis are also preventing the release of alkali chlorides to the flue gas during co-combustion.

Vattenfall Research and Development AB (VRD) has developed the so called ChlorOut concept, for measuring and reducing alkali chlorides in flue gases. The concept consists of an instrument, IACM (In situ Alkali Chloride Monitor), which continuously measures the alkali chloride and SO<sub>2</sub> content in the flue gas and an additive, normally ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), for sulphating the alkali chlorides to alkali sulphates. The flow of the additive is regulated towards a set value for the alkali chloride. During comparative tests ChlorOut has shown more effective in reducing the chlorides deposited on super heaters than co-burning biofuels with other fuels [6], [7].

Variations in CO (carbon monoxide) and NO (nitrogen oxide) are often seen when adding ammonium sulphate to the flue gas. Major decreases in NO levels while

observations of both minor increasing [8] and major decreasing [4] CO levels have been observed.

## **2.1 Aim**

The aim with this diploma work is to evaluate a ChlorOut installation in a CFB (Circulating Fluidised Bed) boiler in Bergkamen Germany. The boiler burns waste wood and has super heater corrosion problems. IACM measurements show very high levels of alkali chlorides in the flue gas.

## **2.2 Method**

Measurements performed within this work are IACM and deposit measurements. Deposit measurements were made with a deposit probe with deposit rings that were exposed to the flue gases and then analysed. The tool for analysis was a SEM/EDX microscope (Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis)

### 3 Literature survey

The literature survey covers questions relevant for a ChlorOut installation in a boiler fired with biofuels. Special weight will be put on sulphur, chlorine and potassium and how they react when present in the deposit of a super heater surface. Since NO and CO are of interest a section will also treat the reactions concerning them.

#### 3.1 Bio-fuel properties

Different bio-fuels consist of different elements such as carbon (C), chlorine (Cl), sulphur (S) and alkali metals (Na, K). The amount of elements present in the fuel decides its properties as a fuel in terms of heat value, ash content, probability for sintering and so forth. As the main goal in this work is to cover problems related to super heater corrosion in bio-fuelled boilers focus will be put on elements concerning these effects. Alkali metals and chlorine are of interest as they form alkali chlorides during combustion and the relation S/Cl in the fuel is of importance from a ChlorOut perspective as it gives a hint of how corrosive the flue gases will be when the fuel is burnt. The contents of the elements in question in different bio-fuels are listed in Table 1.

Table 1: Average properties of different bio-fuels + peat and coal [9]

Elemental analysis					
[% of dry ash free (daf)]				[mg/kg ash]	
	S	Cl	S/Cl	K	Na
Wood	0.03	0.01	3	80 690	4 581
Salix	0.033	0.026	1.3	123 277	2 504
Straw	0.08	0.12	0.7	56 450	6 862
Branches and tops	0.05	0.03	1.7	76 259	8 556
Waste wood (SE)	0.08	0.055	1.5	20 494	14 375
Peat	0.28	0.05	5.6	7 149	2 667
Coal	0.73	0.03	24.3	1 470	560

Table 1 shows that:

- Biofuels are low on sulphur compared to fossil fuels.
- Biofuels have a higher content of alkali metals (Na, K) than peat and coal.
- The relation S/Cl is much higher for peat and coal than for the biofuels.
- Waste wood is the bio fuel with the highest chlorine content besides straw.
- Waste wood has the lowest share of potassium but the highest share of sodium amongst the biofuels

### 3.1.1 Waste Wood

Waste wood (or demolition wood) is the coalition name for recycled wood products such as residues from construction sites, old furniture and other wood based waste. Waste wood contains no residues from the forest industry. Waste wood often contains fairly large amounts of impregnated wood but also wood with paint or other finishing's. Paint can contain zinc and lead that can lead to corrosion problems whilst impregnated wood also contains arsenic, copper and chrome. From construction sites, waste wood is often contaminated with, for example, plastics, metals and stones. Plastic contains chloride that gives waste wood a higher share of fine fraction < 4 mm (~25-40 %) and it is in this fraction that chlorides, alkali metals, zinc and lead are concentrated.

The composition of waste wood can vary widely and the corrosiveness is decided depending on how well the waste is sorted and the amount of impregnated, painted or in other ways chemically treated wood that are present in the fuel [9]. A suggestion on how to reduce the corrosive effect of waste wood is presented in Table 2 [10]. Aside from the fuel the oxygen level is important as reducing conditions has shown to increase alkali related corrosion. Sulphur-containing compounds are also thermodynamically preferred at oxidizing conditions [10], Table 3.

Table 2, Suggestion on how to minimize the combustion problems with waste wood

General measure	Specific measure	The effect of the measure
1) Improving fuel quality	Improved sorting at the source	Reducing the amount of metals and chlorine
	Sieving of the fuel	Separation of fines and thereby reducing the amount of metals
2) Combustion modifications	Avoid reducing conditions at the heat exchanger surfaces	Minimising slagging, fouling and corrosion.
3) Additives or co-combustion	Addition of sulphur with the fuel	Sulphating of troublesome metal chlorides
	Injection of sulphur containing substances in the furnace	Sulphating of troublesome metal chlorides
	Addition of additives or fuels containing silica	Adsorption of troublesome substances

Table 3 Thermodynamic stable condensed zinc and potassium compounds in different temperature intervals

	No Sulphur		Addition of Sulphur	
	Oxidizing conditions	Reducing conditions	Oxidizing conditions	Reducing conditions
700-1000 °C	ZnO		K <sub>2</sub> SO <sub>4</sub> , ZnO	
500-700 °C	KCl, ZnO	KCl, ZnO	K <sub>2</sub> SO <sub>4</sub> , ZnSO <sub>4</sub>	KCl, ZnS

## 3.2 Reactions with K, Cl and S during combustion

The reactions concerning K, S and Cl are important when handling super heater corrosion problems and are therefore treated separately in this chapter.

### 3.2.1 Potassium (K)

Potassium is released during combustion mainly as KCl. It has been shown during combustion of straw that the potassium release to gas phase at temperatures above 500°C correlated with the chlorine concentration in the fuel. Higher temperatures increase the amount of KCl in the gas phase [11]. Knudsen et al. [12] introduces two important parameters concerning the release of potassium during combustion of biofuels, which are K/Si and Cl/K molar ratios. Silicates (Si) have an inhibiting effect on the release of potassium as potassium is easily incorporated in potassium silicates, which are less volatile than for example alkali chlorides. This implies that at high K/Si ratios a higher release of potassium into gas phase can be seen than at low K/Si ratios. This has also been investigated by Jensen et al.[13] and Knudsen [11]. Jensen et al. suggested that potassium silicates are formed by reactions of silicates with KCl. Equilibrium calculations performed by Knudsen for wheat straw show that in silica poor combustion environments potassium is released into gas phase mainly as KOH, KCl and  $K_2SO_4$  whereas in silica rich environments most of the potassium is bound into solid silica compounds. In a silica rich environment where the Cl/K ratio is high the calculations yields an almost complete K release into KCl and no potassium silicates at temperatures over 900°C. This indicates that the Cl/K relation affects the release of potassium more than Si/K.

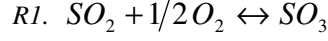
Earth alkali metals e.g. Mg (magnesium) and Ca (calcium) have also shown to have an effect on the release of potassium when burning annual crops. Thy et al. [14] performed measurements showing a much higher release of potassium when the quota (Mg+Ca)/Si was high than low. This is also shown by Knudsen who suggests that calcium and magnesium have stronger bonds to silicon than potassium at increasing temperatures.

### 3.2.2 Chlorine (Cl)

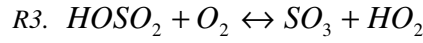
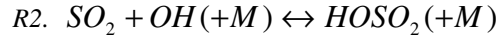
Chlorine is released into gas phase in two steps. Throughout the pyrolysis, below 500°C, chlorine is released as chlorinated hydrocarbons, hydrogen chloride (HCl) or alkali chlorides, mostly potassium chloride (KCl). At temperatures between 400°C and 700°C the release is very small but is then resumed during combustion at temperatures between 700°C and 900°C [11], [15].

### 3.2.3 Sulphur (S)

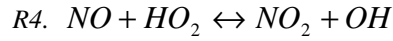
At low temperatures and during oxidizing conditions sulphur is almost completely bound in particles as alkali sulphates. As the temperature rises and in the presence of calcium and silicates the alkali sulphates start to dissociate to sulphur dioxide ( $SO_2$ ). At high temperatures >1000°C most of the sulphur is in the form of  $SO_2$  [11]. Under reducing conditions sulphur may be released as  $H_2S$  or  $S_2$  but under oxygen rich conditions almost all sulphur is bound in the form of  $SO_2$  [15].  $SO_2$  can be oxidized into  $SO_3$  with oxygen as in R1.



The direct reaction R1 between sulphur dioxide and oxygen is, according to Jörgensen et al [16], believed to be too slow to be important for the overall formation of SO<sub>3</sub> during the cooling of the flue gas. They show, under homogeneous conditions, that SO<sub>3</sub> is mainly formed, at temperatures below ~700°C, by the sequence R2, R3.



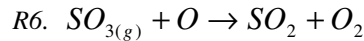
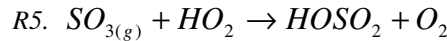
At lower temperatures NO tends to promote formation of SO<sub>3</sub> by reacting with HO<sub>2</sub> as seen in R4 forming OH, which then can react with SO<sub>2</sub> as in R2 [15].



The contribution of NO on the oxidation of SO<sub>2</sub> to SO<sub>3</sub> is according to [15] small.

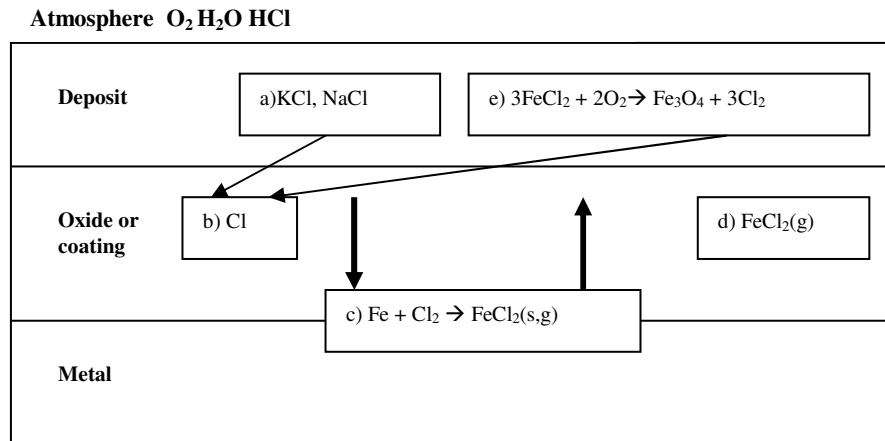
SO<sub>3</sub> can also be formed in the boiler with a catalyst. A known good catalyst for the oxidation of SO<sub>2</sub> is ferric oxide (Fe<sub>2</sub>O<sub>3</sub>). The catalytic effect of iron oxides for SO<sub>2</sub> → SO<sub>3</sub> in fly ash has been investigated by P. Marier et al.[17]. The laboratory study performed showed on a linear increase in the oxidation of SO<sub>2</sub> → SO<sub>3</sub> with increasing amounts of iron oxide in the flue gas at temperatures between 500 - 700°C. Iron oxides on boiler walls and tube surfaces have also been shown to have a catalytic effect on SO<sub>2</sub> → SO<sub>3</sub>. L.A. Hansen et al. [2] suggests this from observations of deposits where alkali chlorides have been sulphated in the deposit to alkali sulphates. This is also supported by Srivastava et al. [18] and Jörgensen et al.[16] Generally, iron oxides have shown high catalytic activity at ~600°C but are active at lower temperatures as well. Its catalytic activity peaks at ~700°C [16].

The consumption of SO<sub>3</sub> often takes place near the flame where oxygen is needed according to reactions R5 and R6. [18]



### 3.3 Chlorine-induced corrosion

Alkali chlorides condense on super heater tubes as sticky melts. Uusitalo.M.A et al. [1] proposes a path for the chlorides when condensed as a melt on a metal surface. The proposed path is described in Picture 1.



Picture 1, A schematic illustration of chlorine circulation in oxidizing environments. The release of gaseous chlorine-containing compounds (a), transport of chlorine through the oxide layer (b), reactions of metal with chlorine (c), evaporation of metal chlorides (d) and oxidation of metal chlorides and release of chlorine back to process (e).

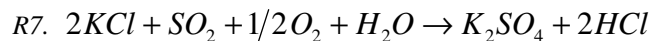
The path is also supported by Salmenoja [19] who has shown that corrosion can take place in deposits containing alkali chlorides even far under the deposits melting point. Salmenoja proposes that the alkali chlorides deposited, release chlorine gas that travels through the iron oxide and forms iron chloride. Iron chloride has high partial pressure at temperatures above 480°C and is transported back through the deposit. When the iron gets in contact with oxygen it is released as iron oxide. The chlorine gas can then once again penetrate the deposit and react with the metal.

Before the chloride penetrates the oxide layer the alkali chlorides can be sulphated in the deposit. As described in chapter 3.2.3 iron oxide has shown high catalytic activity for the oxidation of  $\text{SO}_2 \rightarrow \text{SO}_3$  [16]. As iron oxides are present in boilers on tube surfaces and as particles in the flue gases the reaction is possible. Hansen et al. [2] proposes a reaction path (1-3) for the sulphation of KCl on a super heater tube.



1. Initially, KCl deposits on the super heater surface, e.g., by condensation of gaseous KCl.
2. KCl reacts with  $\text{Fe}_x\text{O}_y$ ,  $\text{FeCl}_2$ ,  $\text{K}_2\text{SO}_4$ , or a fourth (unknown) species and forms a melt phase. This reaction is not unlikely to happen as KCl forms eutectic mixtures with  $\text{FeCl}_2$  (at  $355^\circ\text{C}$ ), with  $\text{K}_2\text{SO}_4$  (at  $690^\circ\text{C}$ ), and possibly also with  $\text{Fe}_x\text{O}_y$ , even though the latter has not been verified.
3. The melted KCl reacts with gaseous  $\text{SO}_3$  and forms  $\text{K}_2\text{SO}_4$ . Gaseous  $\text{SO}_3$  may be present, as  $\text{Fe}_x\text{O}_y$  is known for catalysing the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .

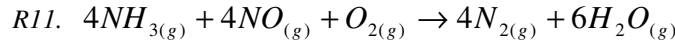
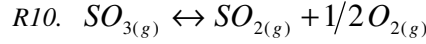
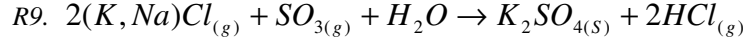
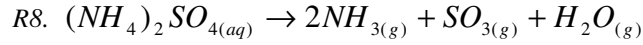
The impact of sulphur on chlorine-induced corrosion has been investigated by Salmenoja K. [19]. Salmenoja measured the ratio S/Cl in the flue gas and found that the risk for corrosion was small at a molar relation  $>4$ , moderate at 2-4 and big at  $<2$ . The active reaction decreasing the corrosion is R7 that yields  $\text{K}_2\text{SO}_4$ , which condense earlier in the boiler, and prevents the chlorine from getting stuck on the super heaters.



Co-combustion tests performed by Vattenfall in a 30 MW<sub>th</sub> CFB boiler showed that a molar ratio S/Cl=6 was needed to reduce the KCl level by 50 %. The high ratio resulted in a rather high concentration of  $\text{SO}_2$  in the flue gas [5]. High concentration of  $\text{SO}_2$  in the flue gas can yield high  $\text{SO}_2$  emissions that increase the risk for low temperature corrosion. The high  $\text{SO}_2$  problem comes from the slow reaction between sulphur dioxide and oxygen in R7. The problem could in theory be avoided by adding  $\text{SO}_3$  directly to the flue gases, which is more reactive than  $\text{SO}_2$ . This is done in the ChlorOut concept.

### 3.4 The ChlorOut concept

The ChlorOut concept aims to reduce the amounts of alkali chlorides (here after expressed as potassium chloride, KCl, as potassium is the most frequent alkali in biofuels) from the flue gases during combustion of biofuels and wastes. The concept consists of an in situ instrument called IACM (In situ Alkali Chloride Monitor), which measures the content of KCl and  $\text{SO}_2$  in the flue gas and a sulphur-containing additive that is sprayed on the flue gases up stream the super heaters. The sulphate flow is often controlled by the IACM measurements to a set KCl level. The additive used is a solution of ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , which is decomposed to  $\text{SO}_3$  and  $\text{NH}_3$  according to R8. From a ChlorOut perspective the important product is  $\text{SO}_3$  that reacts with alkali chlorides in the flue gas according to R9.  $\text{SO}_3$  is in equilibrium with  $\text{SO}_2$  and  $\text{O}_2$  in the boiler (R10) and the rate constant for the reaction is pushed toward  $\text{SO}_3$  due to oxidizing conditions. By adding  $\text{SO}_3$  directly to the flue gases the alkali chlorides are more effectively reduced than by adding sulphur to the fuel and the increased  $\text{SO}_2$  emissions are smaller [5]. An extra effect when adding ammonia to flue gases is reduction of NO in the so-called SNCR reaction (R11).



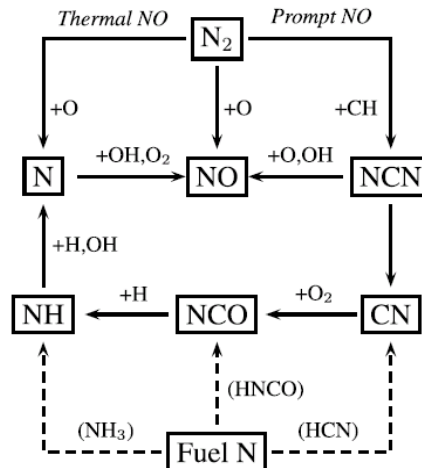
As mentioned in chapter 3.2.3, SO<sub>2</sub> can be oxidized to SO<sub>3</sub> with iron oxides as catalyst. This reaction should in theory increase with increasing SO<sub>2</sub> why a relation between SO<sub>2</sub> and KCl in the flue gas and the chlorine content in deposits should be interesting. This has so far not been done.

### 3.5 Nitrogen oxide

#### 3.5.1 Formation of nitrogen oxide

Nitrogen oxides are formed during all combustion with oxygen. There are two main sources of formation; either by fixation of molecular nitrogen in the combustion air or by oxidation of fuel bound nitrogen. Formation of NO during FBC (Fluidised Bed Combustion) mainly originates from oxidation of fuel bound nitrogen [20] and therefore will fixation from molecular nitrogen not be further treated.

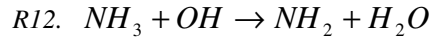
The release of fuel bound nitrogen is more complex than the release from the combustion air and not yet completely understood. For solid fuels nitrogen can either be released with the volatiles during pyrolysis or remain in the char. The char bound nitrogen undergoes heterogeneous oxidation to NO or evolves as light components as NH<sub>3</sub>. Picture 2 shows a simplified overview of the reaction path for nitrogen during combustion [15]. Limiting factors for the formation of nitrogen oxides are mainly the amount of fuel bound nitrogen and the oxygen level in the combustion chamber. A high oxygen level promotes the NO formation while a fuel rich environment promotes conversion of reactive nitrogen species to N<sub>2</sub>. [15]



Picture 2, Simplified reaction path diagram for the formation of nitrogen oxide (NO) during combustion. [15]

### 3.5.2 Reduction of NO

NO is mainly reduced in combustion processes by the SNCR (Selective Non-Catalytic Reduction) or the SCR (Selective Catalytic Reduction) technology. During conventional SNCR, ammonia or urea is injected to the boiler at a flue gas temperature above 800°C. NO is then reduced through reactions R12 and R12b.



## 3.6 Carbon monoxide

CO is formed during all combustion of carbon under oxygen lean conditions and can be oxidized into CO<sub>2</sub> with OH radicals as in R13.



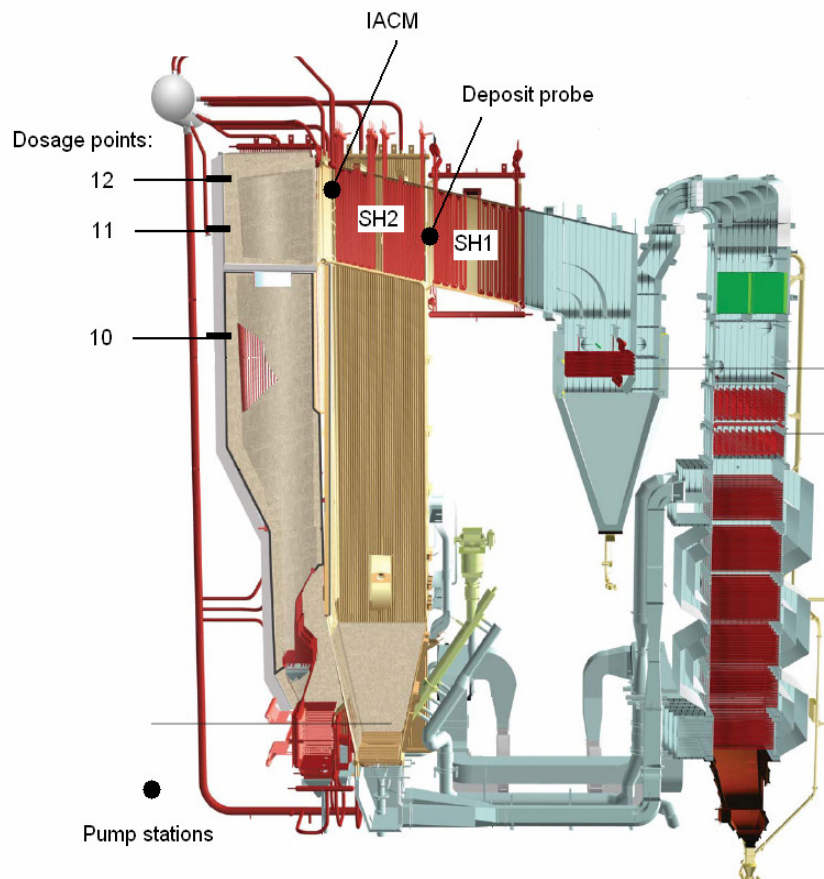
CO competes with other compounds for the OH radicals that can inhibit the oxidation of CO. Predicted results on CO oxidation with 5 % O<sub>2</sub> indicates that NO has a promoting effect on the CO oxidation below 780°C. Under reducing conditions NO has shown to inhibit the oxidation [15]. When adding ammonia or urea CO often increases [8] as ammonia competes with CO for the OH radicals as can be seen in R12. SO<sub>2</sub> has also shown an inhibiting effect on the CO oxidation in CFB boilers by interacting with the OH radical pool. The interaction is rather complicated and is described by reference [15]. The work on the area continues as recent results [15] show that addition of small amounts of sulphur to the combustion of low-sulphur fuels has enhanced the oxidation of CO. The presence of HCl in the flue gas has both shown to have an inhibiting and a promoting effect on the CO oxidation [15].

Results from experiments by Hindiyarti et al. [21] show that CO oxidation strongly depends on the KCl level in reducing conditions. When KCl was fed to the CO oxidation system the CO oxidation dramatically went down and when the feeding was ended the oxidation rate went up. This strongly indicates that KCl has an inhibiting effect on the CO oxidation.

## 4 Experimental

### 4.1 Plant description

The investigated boiler is situated in Bergkamen, mid-west Germany. The boiler is a  $20 \text{ MW}_{\text{el}}/\sim 58 \text{ MW}_{\text{th}}$  CFB from Foster Wheeler [22] without flue gas condensation. The boiler produces steam from mainly waste wood to the turbine with a flow of  $22 \text{ kg/s}$  (90 bar,  $500^\circ\text{C}$  (final SH temp from INTREX)). The electrical efficiency of the turbine is 35 %. The outgoing flue gas temperature from the stack is around  $150^\circ\text{C}$ . Picture 3 shows a schematic picture of the Bergkamen boiler. The boiler is constructed with two super heaters after two cyclones and two INTREX's at the bottom of the cyclones. Super heater 1 and 2 are respectively made of steel 13CrMo44 (SS2216) and 10CrMo910 (SS2218). Average outgoing steam temperature in SH2 and SH1 is approximately  $390^\circ\text{C}$  and  $375^\circ\text{C}$  respectively. The super heaters are continuously cleaned with a soot blower using process steam. The soot blowing in Bergkamen were, during the tests, performed approximately every 3-4 hours.



Picture 3, Schematic picture of a CFB boiler with Foster Wheeler design [22]. Location of equipment and dosage points are noted in the picture.

## 4.2 ChlorOut system in Bergkamen

The temporary ChlorOut installation in Bergkamen consists of a container for the ammonium sulphate, two pumping units for pumping the sulphate in to the boiler, regulators to regulate air and water pressure, lances with 6 hole nozzles for an even distribution of the sulphate in to the boiler and an IACM instrument which continuously measured alkali chloride and  $\text{SO}_2$  in the boiler. The location of the different parts of the ChlorOut system is shown in Picture 3 (above). A more thorough description of the parts follows.

### 4.2.1 Pump stations

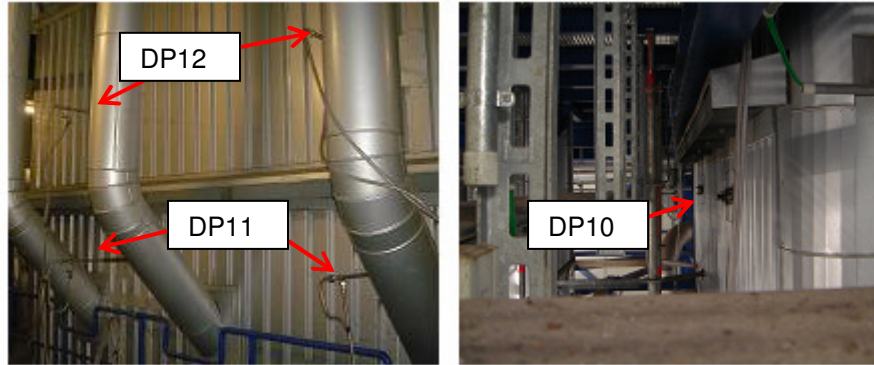
Two pump stations (each as shown in **Error! Reference source not found.**) were placed on the ground floor in the boiler house together with the ammonium sulphate tanks. The flows of the pump stations were controlled either by motor frequency regulation or by a flow meter. The pumps were connected to one dosage point each. The tanks used during operation within this work were temporary one cubic meter storage tanks. For long-term operation a bigger tank will most likely be selected. The sulphate was pumped through armoured rubber tubes to the dosage points.



Picture 4, Pump station for ammonium sulphate

#### 4.2.2 Dosage points

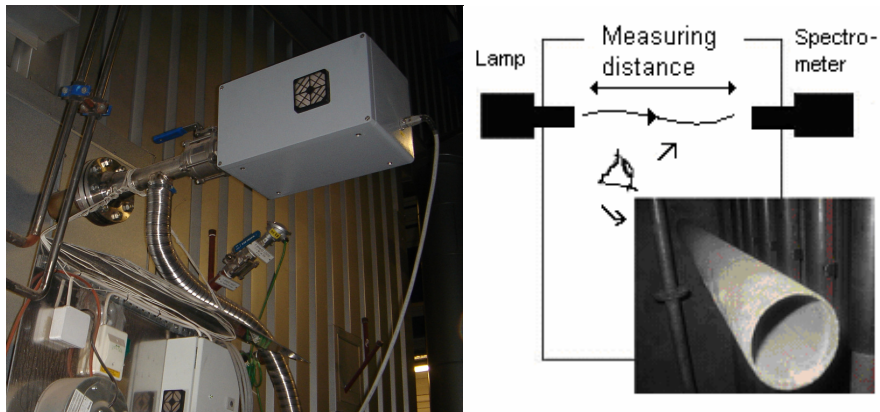
During the measurements in Bergkamen different dosage points were investigated. Two of the points, 11 and 12, were placed above the cyclone and one, 10, in the upper part of the cyclone as can be seen in Picture 3 and Picture 5. Each dosage point consisted of two lances, one in each cyclone. The distance from dosage points 11 and 12 to super heater 2 is approximately 5 meters.



Picture 5, Dosage point 12 and 11 (left) and 10 (right)

#### 4.2.3 IACM, *In situ Alkali Chloride Monitor*

The IACM instrument was placed in an available opening between dosage point 12 and super heater 2 in the boiler. The opening was not ideal for the instrument but had to be used since no new opening could be made. The instrument was placed high up, near the ceiling, in the space after the cyclones (see Picture 3). The measuring distance for the instrument was reduced in order to get more accurate measurements. The reduction was done with steel pipes inside of the boiler as in Picture 6. A further description of the instrument and its functions will be included later in this chapter.



Picture 6, IACM instrument (left) and pipe to shorten IACM measuring distance (right)

### 4.3 Test plan

The measurement campaigns in Bergkamen were performed at two different occasions during week 42 and 44, 2007. They will hereafter be named test period 1 and 2 (TP1 and TP2). Measurements were performed during the test periods with IACM and deposit probes further described in chapter 4.4. The plant measuring system continuously collected operational data. The tests periods were three hours during TP1 and six hours during TP2. Varying parameters during the tests were:

- Oxygen level: Normal ( $O_2 = \sim 4\%$ ) and High ( $O_2 = \sim 5\%$ )
- Dosage points: Position 10&12 or 11&12
- Sulphate flow (total): 50-100 l/h
- Deposit ring temperatures: TP1 375°C, 425°C and 500°C  
TP2 425°C, 475°C and 540°C

The oxygen level was varied to evaluate if an increase in oxygen level would improve the sulphation of KCl. The cause for varying dosage point was to investigate the influence of residence time and mixing. Dosage point 10 was evaluated with the purpose of a better reduction due to longer residence time and a better mixing of the flue gases and the sulphate in the cyclone. The ammonium sulphate flow was varied in the different tests (“ChlorOut tests” and “Reference tests” = no flow) to see how the KCl level in the flue gas and the composition of the deposits responded to different flows. Of interest was also levels of NO and CO during the ChlorOut and reference tests.

#### 4.3.1 Test period 1

The tests during TP1 were carried out during a period of three hours. The test schedule can be seen in Table 4. The tests were timed so that no soot blowing was performed during the tests. The purpose with the tests was to see how the composition of the deposits responded to the different flows, dosage points, temperatures and oxygen levels. The ring temperatures were selected to simulate the actual- ( $\sim 425^\circ\text{C}$ ), above the actual- ( $500^\circ\text{C}$ ) and under the actual- ( $375^\circ\text{C}$ ) metal temperature of the Bergkamen super heaters.

Table 4 Test schedule during TP1, (3-hour tests)

Test	Ammonium sulphate flow [l/h]	Dosage points	$O_2$ [%]
T1 ref.	0	-	Normal
T2	25 + 25	11 & 12	Normal
T3	50 + 50	10 & 12	Normal
T4	50 + 50	10 & 12	High
T5 ref.	0	-	High
T6	50 + 50	11 & 12	Normal
T7	25 + 50	11 & 12	Normal
T8 ref.	0	-	Normal

#### 4.3.2 Test period 2

The tests during TP2 were carried out during a period of six hours. The test schedule can be seen in Table 5. The purpose with the prolonged tests was to see how the sulphate affected the corrosion on the super heaters in the boiler. Ring temperatures were chosen to enhance the corrosion. When starting TP2 it was revealed that no consideration could be taken to the soot blowing. This aspect will be considered when evaluating the results as the soot blowing most certainly would affect the deposits on the deposit probe.

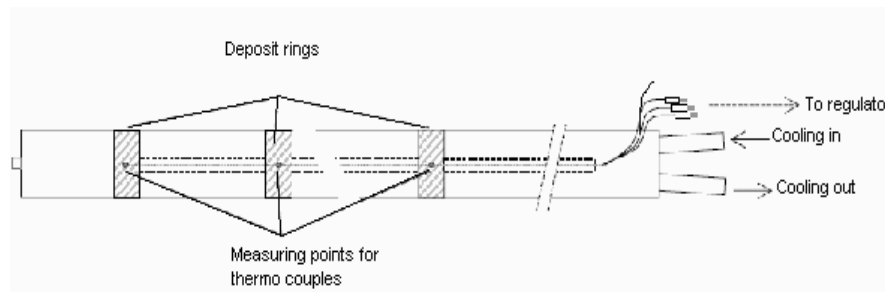
Table 5, Test schedule during TP2, (6-hour tests)

Test	Ammonium sulphate flow [l/h]	Dosage points	O <sub>2</sub> [%]
T9 ref.	0	-	Normal
T10 ref.	0	-	Normal
T11	50 + 50	11 & 12	Normal
T12	25 + 50	11 & 12	Normal

### 4.4 Measuring methods

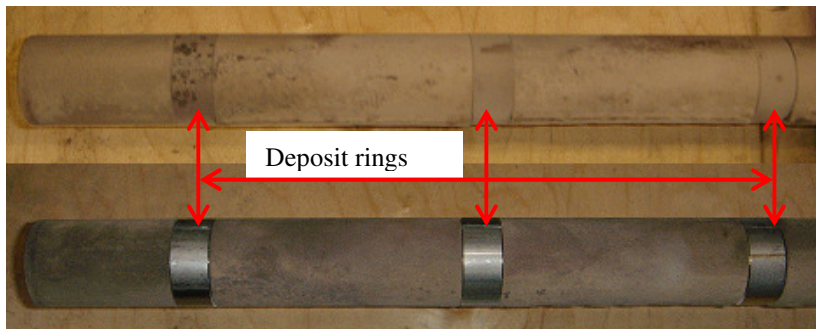
#### 4.4.1 Deposit measurements

The purpose with the deposit measurements was to investigate what in the flue gas that would condense on the super heaters at certain temperatures during operation. The deposit measurements were performed with a deposit probe between super heater 2 and 1 (see Picture 3). The deposit probe that was used collects deposits on three separately cooled steel rings. Two different steels were used during the measurements, 10CrMo910 (SS2218) and 304L (SS2333). 304L was used during the 3-hour tests as it does not contain any molybdenum, which easily is confused with sulphur in the SEM/EDX microscope and could disturb the elemental analysis. During the 6-hour test 10CrMo910 was used as it is the steel used in SH2. The cooling medium to the probe was high-pressure air and the flow was regulated with a PID regulator towards the set value of the ring temperature given by thermo couples at each ring. During measurements the deposit probe was inserted approximately one meter into the boiler. The deposit rings were then located 0.60, 0.75 and 0.90 meters from the inner wall of the boiler. A schematic picture of a deposit probe and a description of its features is shown in Picture 7 below. Picture 8 a-c shows the deposit probe and the control unit used in Bergkamen.

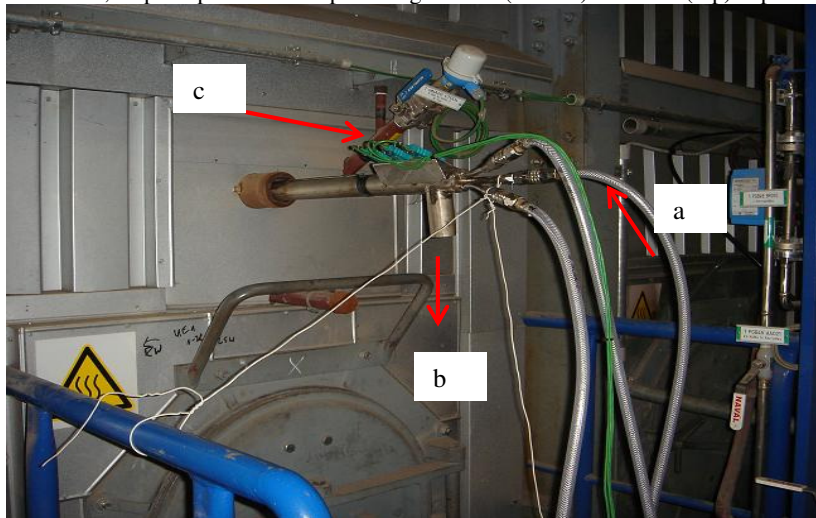


Picture 7, Schematic picture of the deposit probe used during deposit measurements.

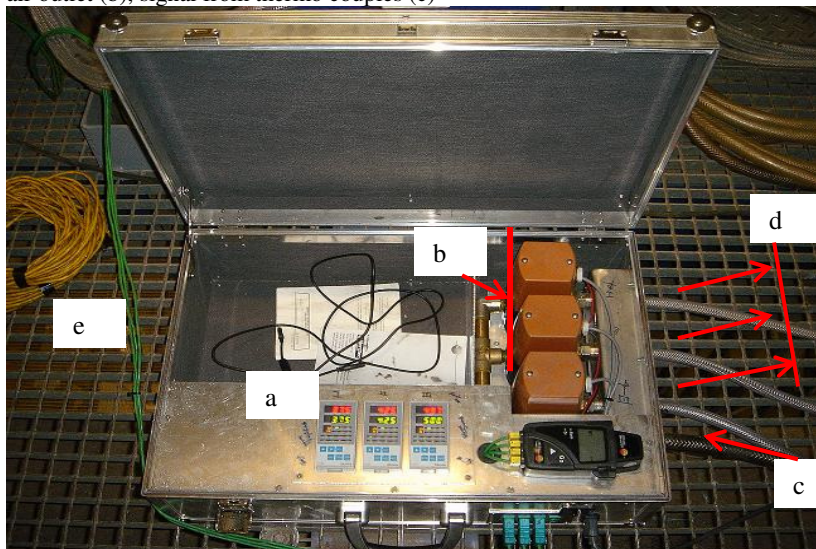




Picture 8a, Deposit probe with deposit rings before (bottom) and after (top) exposure.

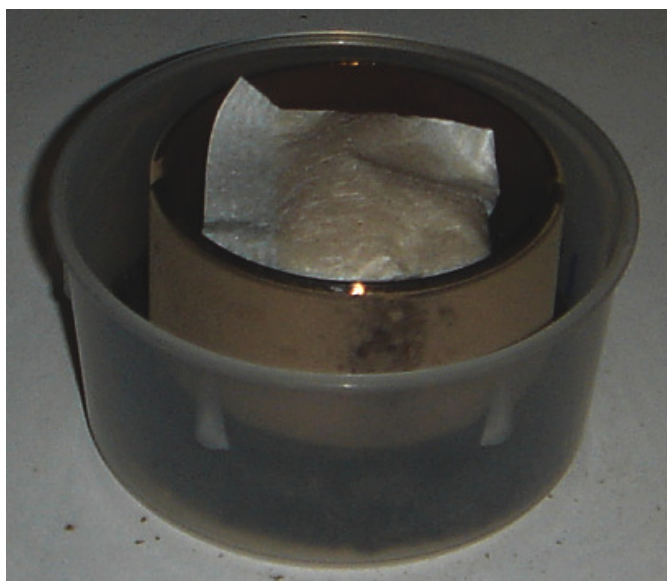


Picture 8b, Deposit probe during measurement in Bergkamen. Cooling air inlet (a), cooling air outlet (b), signal from thermo couples (c)



Picture 8c, Regulator box. Control unit for each ring (a), regulators (b), cooling air inlet (c), cooling air outlet (d), signal from thermo couples (e).

Before the measurements could be performed the rings were cleaned to avoid contamination and weighed. The rings were given a specific id-number and stored in plastic containers until the exposure. The system for identification was simple. Rings of material 304L was given number 1-25 while rings of material 10CrMo910 was given number 60-71. Rings with number 1-25 were used during TP1 and rings with number 60-71 were used during TP2. After exposure the rings were again stored in the same container with a drying bag to ensure that no moist would penetrate the deposit, Picture 9. The rings measured 48 x 20 x 2 mm.



Picture 9, Deposit ring in storage container with drying bag after exposure to flue gas.

#### 4.4.2 IACM measurements

Measurements of alkali chlorides ( $\text{KCl}+\text{NaCl}$ ) and  $\text{SO}_2$  in gas phase were performed with an *In-situ Alkali Chloride Monitor*, IACM developed by Vattenfall Research & Development AB. The IACM uses molecular absorption spectroscopy to detect and measure the amount of alkali chlorides and  $\text{SO}_2$  in flue gases. The instrument consists of two major parts, one light emitter (xenon lamp) and one light receiver (spectrometer) and is placed cross stack prior to the super heaters in the boiler. The xenon lamp emits light through the stack and the intensity of the light in the UV spectra received at the spectrometer side is then measured. By comparing the measured spectra with reference spectra from calibration in controlled environments and from the difference in intensity the concentration of alkali chlorides is achieved. IACM has normally a sampling time of 5-10 seconds and the detection limit at a 5 meter measuring distance is 1 ppm for  $\text{KCl}+\text{NaCl}$  and 4 ppm for  $\text{SO}_2$ . The IACM measurements were performed continuously throughout the test periods.

#### 4.4.3 Operational data

Data for operating conditions were obtained from the plants own measuring systems. These data include among others, boiler loads, various temperatures, levels of NO, CO, HCl, SO<sub>2</sub> and O<sub>2</sub>. SO<sub>2</sub> and O<sub>2</sub> were measured directly after the super heaters while HCl, NO and CO was measured after the flue gas filter prior to the stack.

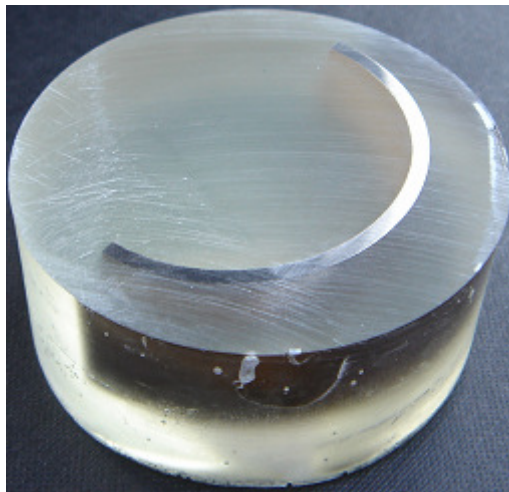
### 4.5 Analytical methods

#### 4.5.1 SEM/EDX analyses

SEM/EDX, short for “Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis”, is used to analyze surfaces of solid objects with higher resolution than optical microscopy. It also provides X-Ray Analysis without damaging the sample. It is, with a SEM/EDX microscopy, possible to detect and locate different elements on samples being analyzed. The SEM/EDX analyses within this diploma work were performed with a Hitachi S-3000N Scanning Electron Microscope at the University of Gävle.

Two different types of analyses were performed: Elemental analysis and cross-sectional analysis. In the elemental analysis the elemental compositions of the deposits were determined. Before the elemental analysis the deposit rings had to be prepared to fit in the microscope. During preparation the rings were divided in two equally big parts with a saw. Analyses were then performed on the wind and lee side of the rings regarding all detectable elements in the deposit.

To know where in the deposit specific elements were located a so-called cross-section analysis of selected rings were performed. In this way it was possible to determine where, in relation to the ring surface, certain elements were located. Before analyses could be done the ring halves had to be enclosed in epoxy and polished so that a clean and smooth metal and deposit surface could be analysed.



Picture 10, Deposit ring prepared for cross-section analysis.

## 5 Results

The results from the Bergkamen tests will be presented in this chapter in two separate sections: TP1 and TP2. Table 6 and Table 7 show the test plan for both test periods. The 3-hour tests were performed between 16 and 18/10 2007 and the 6-hour tests between 29 and 30/10 2007. “O<sub>2</sub> average” is an average during each test. The tests were performed with normal oxygen levels except test T4 and T5 ref. where the oxygen level was increased. In test T3 and T4 dosage point 10 was tested. The fuel during all tests was waste wood. As the composition of the waste wood used is not specified variations in data between equal test series can be seen.

Table 6, Test plan for TP1

Test	Ring number			Date	Time	Flow [l/h]	Dosage points	O <sub>2</sub> average [%]
	375°C	425°C	500°C					
T1 ref.	1	2	3	2007-10-16	12:00-15:00	0	-	4,2
T2	4	5	6	“	18:15-21:15	25+25	11&12	4,3
T3	7	8	9	2007-10-17	10:07-13:10	50+50	10&12	4,2
T4	10	11	12	“	15:17-18:17	50+50	10&12	5,2
T5 ref.	13	14	15	“	19:26-22:26	0	-	5,1
T6	16	17	19*	2007-10-18	10:22-13:22	50+50 (150)**	11&12	4,4
T7	20	21	22	“	14:47-17:47	25+50	11&12	4,4
T8 ref.	23	24	25	“	19:00-22:00	0	-	4,3

\*Ring 18 was not used,

\*\*Flow meter failure, 150 l/h was the actual flow in point 12 during test T6

Table 7, Test plan for TP2

Test	Ring number			Date	Time	Flow [l/h]	Dosage points	O <sub>2</sub> average [%]
	425°C	475°C	540°C					
T9 ref.	60	61	62	2007-10-29	09:55-15:55	0	-	4,4
T10 ref.	63	64	65	“	16:25-22:25	0	-	4,3
T11	66	67	68	2007-10-30	08:55-14:55	50+50	11&12	4,4
T12	69	70	71	“	15:35-21:23	25+50	11&12	4,5

## 5.1 Test period 1

### 5.1.1 Operational data

Results from a selection of parameters from the power plants own measurement system during the tests are presented in Table 8 and Table 9. The average load during the tests was in general stable and the boiler was operated at maximum load. Temperatures were also stable with a slight indication of decreased temperature in the boiler when the oxygen level was above normal (T4, T5 ref.).

Table 8, Average operational data during TP1

	T1 ref.	T5 ref. High O <sub>2</sub>	T8 ref.	T2	T3	T4 High O <sub>2</sub>	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11%12
Bed temp. [°C]	817	795	814	810	811	802	808	814
Steam temp. SH 1 [°C]	370	377	376	375	374	376	373	375
Steam temp. SH 2 [°C]	387	385	385	385	385	385	385	385
Temp. above cyclone [°C]	824	800	815	819	811	802	814	819
Temp. before SH2 [°C]	742	729	735	744	734	730	730	733
Temp. after SH2 [°C]	587	586	582	590	584	591	583	582
Steam load [kg/s]	22.6	22.5	22.2	22.6	22.6	22.5	21.8	22.3
Electrical load [MW]	20.0	20.0	19.7	20.0	20.0	20.0	19.4	19.8

Table 9, Average values of SO<sub>2</sub>, CO, NO and O<sub>2</sub> during TP1

	T1 ref.	T5 ref. High O <sub>2</sub>	T8 ref.	T2	T3	T4 High O <sub>2</sub>	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11%12
SO <sub>2</sub> [mg/m <sup>3</sup> ]	197	152	251	197	160	122	230	225
CO [mg/m <sup>3</sup> ]	13	19	17	44	54	28	60	25
NO [mg/m <sup>3</sup> ]	112	114	93	63	32	53	28	58
O <sub>2</sub> [%]	4.2	5.1	4.3	4.3	4.2	5.2	4.4	4.4

#### 5.1.1.1 SO<sub>2</sub>, CO and NO

NO drops as previewed during the ChlorOut tests due to reaction R11 and the overall trend is that CO rises somewhat when adding ammonium sulphate to the flue gas. This could possibly be explained by increased competition for OH radicals as described in 3.6. Position 10 seems to have an inhibiting effect on the CO oxidation but it is hard to predict if the high CO level in test T3 is entirely due to the dosage point. The increased oxygen level in T4 lowers CO and increases NO, compared to T3. Test T6 also shows a high CO level indicating that high ammonium sulphate flows also could result in somewhat higher CO levels. There is a slight indication that position 11 gives higher SO<sub>2</sub> levels than position 10. When increasing the oxygen level in test T4 the test shows even lower SO<sub>2</sub> levels than the reference tests. A reduction in SO<sub>2</sub>, when increasing the oxygen level, can also be observed in T5 ref.

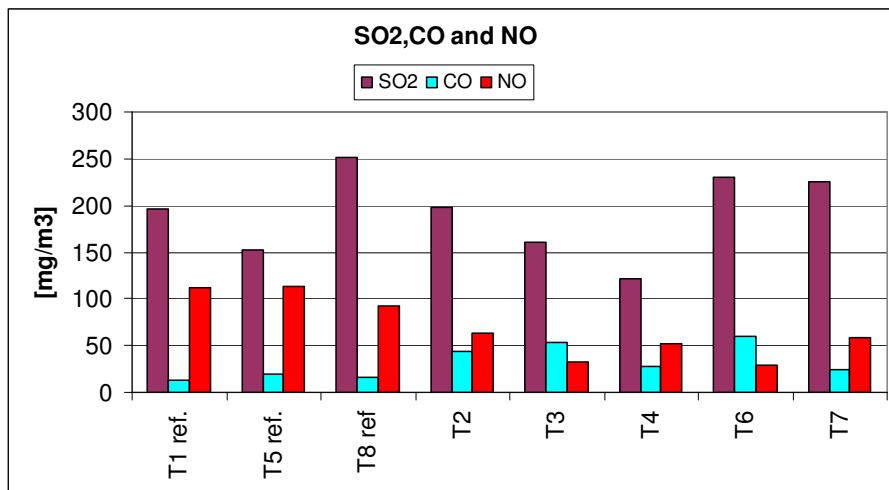


Figure 1, SO<sub>2</sub>, CO and NO in boiler during TP1

*The results from the chapter could be summarized as follows: NO decreases and CO increases during the ChlorOut tests compared to the reference tests. SO<sub>2</sub> varies somewhat but with no clear trend.*

#### 5.1.2 IACM

The IACM measurements reveal that an increased dosage of ammonium sulphate to the flue gases lowers the amount of KCl and slightly increases the amount of SO<sub>2</sub> in the IACM region. KCl drops from approximately 200 ppm to 40-80 ppm, depending on the ammonium sulphate flow. SO<sub>2</sub> increases from an average of 32 ppm (references) to a maximum of 61 ppm (T6). The results are presented in Table 10 and Figure 2. The increased oxygen level in test T4 and T5 ref. does not seem to have any major effect on the KCl or SO<sub>2</sub> level in the super heater region of the boiler. The results do not reveal whether dosage point 10 or 11 better reduces KCl. If comparing T3 and T7 the KCl level in T3 is higher than in T7 even though a higher sulphate flow was used in T3, indicating that the reduction should be better when dosing in 11 than in 10. The slightly increased SO<sub>2</sub> level (Figure 2), seen in

all ChlorOut tests, is probably due to the increased activity of reaction R10 whose equilibrium is pushed towards the  $\text{SO}_2$ ,  $\text{O}_2$  side due to the increase in  $\text{SO}_3$ . The big variation in data for T8 ref., also seen in 5.1.1.1 is probably due to variations in fuel composition.

Table 10, Average results of IACM measurements during test in TP1.

	T1 ref.	T5 ref. High $\text{O}_2$	T8 ref.	T2	T3	T4 High $\text{O}_2$	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11&12
$\text{SO}_2$ [ppm]	29	23	36	40	46	38	61	45
KCl [ppm]	220	227	171	161	83	75	42	55

After test T6 a problem with one of the pump stations were discovered. The test was planned to be a 50+50 l/h test but the flow meter on the pump station had a failure. The 150 l/h marked in the test schedule is calculated from markings on the ammonium sulphate tank before and after the test and is close to what actually was the flow in point 12 during test T6. After test T6 the flow was measured manually to ensure a reliable flow. Manual measurements were performed with timer and container of known volume and then evaluated and repeated until the right flow was obtained. The failure has given test T6 a different look compared to the other tests. T6 has higher  $\text{SO}_2$  level than KCl indicating a high KCl reduction but also a high  $\text{SO}_2$  slip out of the super heater region (Figure 2).

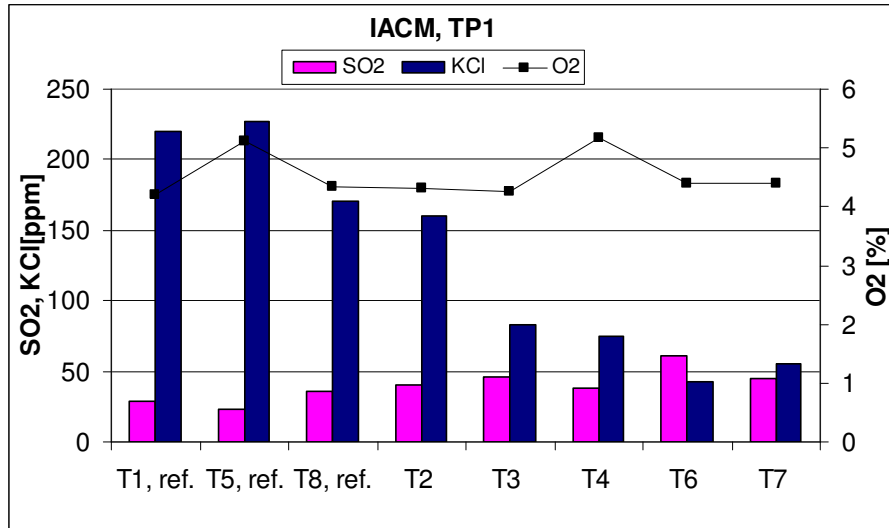


Figure 2, Average values of  $\text{SO}_2$ , KCl and  $\text{O}_2$  during the 3-hour tests

The IACM response on KCl due to the ammonium sulphate is instantaneous both when dosing in position 10&12 and 11&12. Trends for KCl and  $\text{SO}_2$  for all the tests during TP1 are presented in Appendix 1. Figure 3 shows IACM measurements during tests T3, T4 and T5 ref. (17/10 2007).



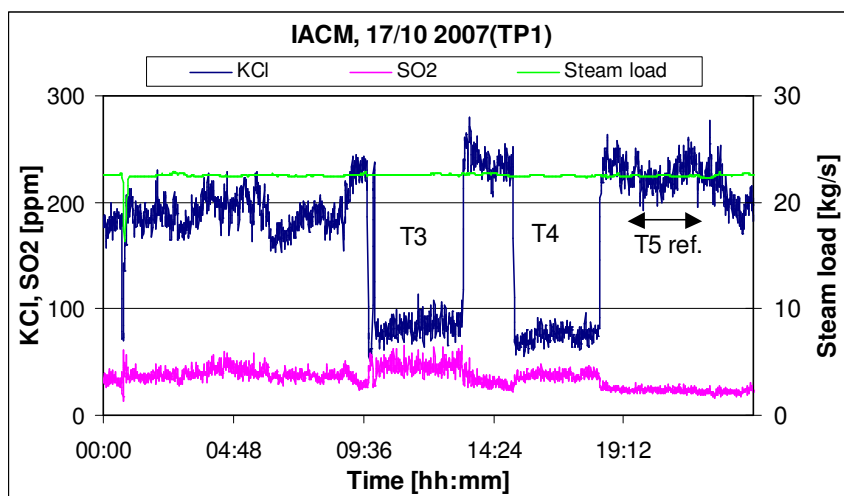


Figure 3, IACM measurements 2007-10-17

The results reveal that it is possible to measure the alkali chloride level in situ. The measurements show that KCl is reduced and that SO<sub>2</sub>, measured by the IACM, increases somewhat during the ChlorOut tests. The response to the dosage is instantaneous except during test T2 that also is the tests with the least decrease in KCl, probably due to a not sufficient flow.

### 5.1.3 Deposit growth

The deposit growth is measured by weighing the rings before and after exposure to the flue gas. The results are presented in Table 11. The three reference tests show the same trend with the highest deposit growth at 500°C and the lowest at 425°C. The ChlorOut tests have in general the highest growth at 375°C and the lowest at 425°C. Figure 4 show a bar chart of the deposit growth during TP1. The low growth rate during T6 and the high during T2 indicate that the sulphate flow matters for the growth rate of the super heater deposits. The deposit growth seems to depend more on the choice of dosage point than oxygen level. T3 and T4 have equal growth rate while T7 has somewhat lower even though a lower sulphate flow was used in T7.

Table 11, Deposit growth rate [g/m<sup>2</sup> h], TP1

	T1 ref.	T5 ref. High O <sub>2</sub>	T8 ref.	T2	T3	T4 High O <sub>2</sub>	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11%12
Growth rate at:								
375°C	6.1	9.7	5.3	8.6	6.3	6.3	3.4	4.2
425°C	5.7	8.3	3.3	6.7	3.7	4.3	2.7	2.9
500°C	12.2	14.1	14.3	6.0	5.0	4.8	2.9	4.2



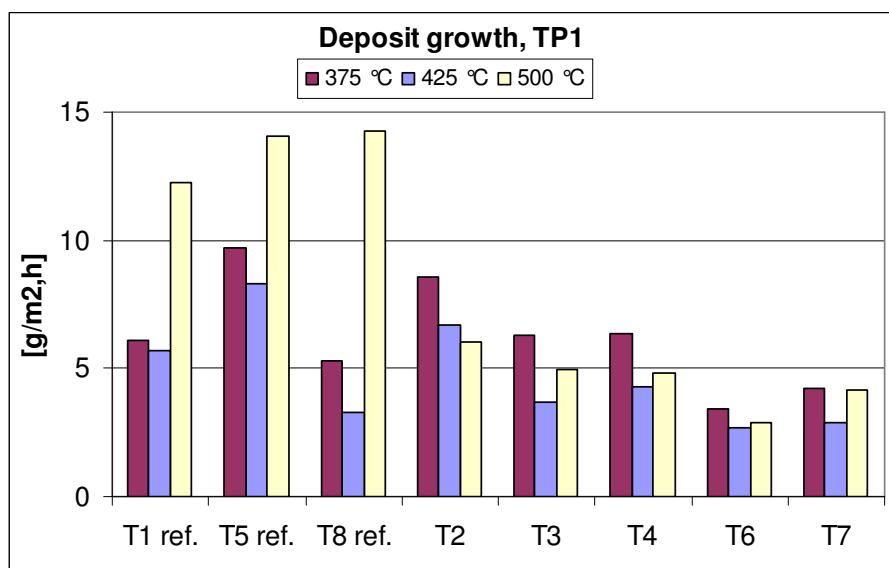


Figure 4 Deposit growth rate [g/m<sup>2</sup>·h] on deposit rings from TP1.

*Results from the chapter show that the effect of ammonium sulphate on the deposit growth is clearest at 500°C. At 425°C the flow in T2 is not sufficient to lower the growth rate and at 375°C are tests T6 and T7 the only that are significantly lower than the reference tests.*

#### 5.1.4 Elemental analysis

The elemental analyses were performed on all detectable elements in the deposits on the wind and lee side of the rings. The complete results from the analyses are shown in Appendix 2. This section mainly focuses on chlorine (Cl), sulphur (S) and sodium + potassium (Na+K). Table 12 show the results for tests during TP1.

Table 12 Cl, S and Na+K in deposits on wind and lee side of rings from TP1. Values in weight -% of the deposit.

Ring nr.	Test	Wind				Lee		
		Cl	S	Na+K		Cl	S	Na+K
	T1 ref							
1	375°C	20.7	4.4	18.9		6.6	2.3	2.4
2	425°C	12.9	2.7	11.6		5.9	1.8	1.7
3	500°C	2.3	2.3	2.9		4.9	3.0	4.0
	T2 25+25 l/h, 11&12							
4	375°C	10.9	9.6	5.6		5.1	2.6	1.7
5	425°C	5.2	12.8	10.9		4.3	3.8	3.0
6	500°C	6.4	11.0	7.4		4.2	3.1	2.4

		Wind			Lee		
Ring nr.	Test	Cl	S	Na+K	Cl	S	Na+K
	T3 50+50 l/h, 10&12						
7	375°C	3.7	17.2	16.2	1.6	4.0	4.1
8	425°C	2.3	13.7	13.0	1.4	4.0	4.1
9	500°C	1.6	15.3	2.8	1.0	4.1	4.4
	T4 50+50 l/h, 10&12						
10	375°C	4.3	14.3	13.4	3.3	4.2	3.8
11	425°C	3.2	13.5	11.2	1.1	2.7	3.6
12	500°C	8.8	11.1	8.0	1.3	2.5	3.3
	T5 ref.						
13	375°C	14.1	2.3	12.3	5.0	1.2	1.2
14	425°C	10.8	2.1	6.3	3.7	1.1	1.2
15	500°C	3.7	2.4	3.6	7.9	1.4	2.2
	T6 50+150 l/h, 11&12						
16	375°C	0.8	16.0	16.6	0.9	3.5	5.1
17	425°C	0.7	14.8	15.4	0.7	4.3	4.9
19	500°C	0.0	15.2	12.8	0.5	5.9	5.8
	T7 25+50 l/h, 11&12						
20	375°C	2.9	13.4	13.2	5.2	5.6	5.0
21	425°C	3.7	8.9	9.1	0.9	3.2	4.4
22	500°C	2.5	10.0	5.3	1.7	4.5	5.0
	T8 ref.						
23	375°C	2.8	3.4	4.3	1.6	3.4	3.6
24	425°C	17.7	6.2	17.0	1.0	3.2	3.9
25	500°C	19.1	4.8	15.8	4.2	4.0	4.2

The elements investigated (Cl, S, Na+K) clearly vary between wind and lee side of the ring. The wind side has in general higher shares of the elements examined. When observing the total elemental composition in Figure 5 the lee side consists of more iron and chromium than the wind side. This is due to the thinner deposits on the lee side, which also could be observed during handling of the rings (Picture 11) i.e. the high shares of iron and chromium originates from the ring. This gives less accurate results from the lee side of the rings.

If excluding iron and chromium as in Figure 6 the difference between wind and lee is not very big regarding deposit composition except for potassium, which is found in smaller quantities on the lee side than on the wind side. Potassium and sodium does not follow the same trend as the deposits consist of equal shares of sodium.



Picture 11, Ring 13 (375°C) from test T5 ref. lee side (left) and wind side (right)

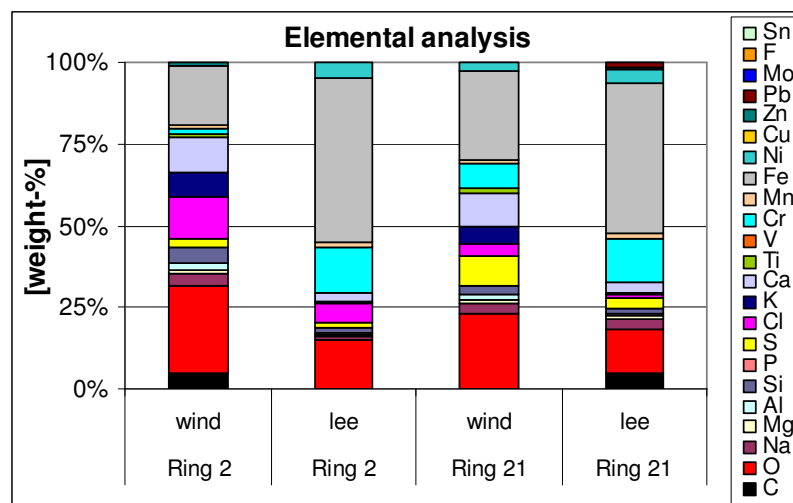


Figure 5, Elemental analysis of ring 2 (T1 ref., 425°C) and ring 21 (T7, 425°C)

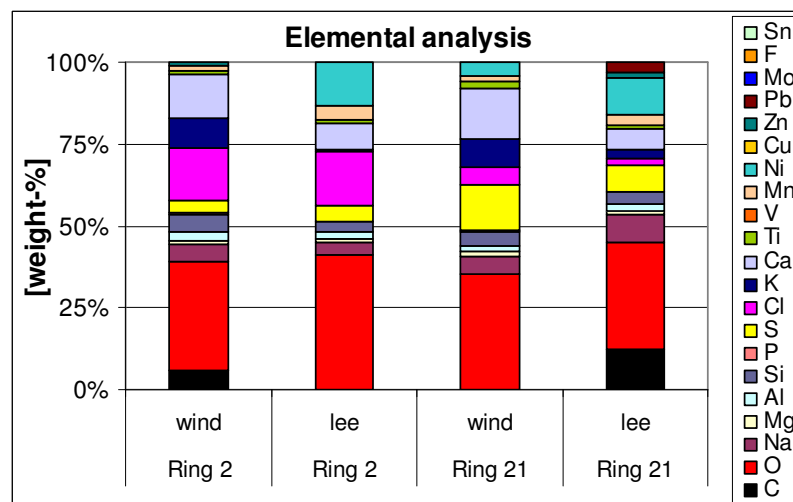


Figure 6, Elemental analysis of ring 2 (T1 ref., 425°C) and ring 21 (T7, 425°C), Iron and chromium excluded.

#### 5.1.4.1 Wind-side

Figure 7 shows that the chlorine content in the wind-side deposits from the ChlorOut tests has radically decreased and the sulphur has increased compared to the reference tests. The amount of Na+K varies between the tests and it is not possible to see any correlation between the Na+K content in the deposits and the flow of ammonium sulphate. To compare the sulphation of the deposits during the different tests a relation S/Cl in the deposits were calculated. The result is shown in Table 13.

Table 13, Relation S/Cl from wind side deposits during TP1

	T1 ref.	T5 ref. High O <sub>2</sub>	T8 ref.	T2	T3	T4 High O <sub>2</sub>	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11%12
S/Cl 375°C	0.2	0.2	1.2	0.9	4.6	3.3	19.1	4.6
425°C	0.2	0.2	0.4	2.5	5.9	4.3	21.7	2.4
500°C	1.0	0.7	0.3	1.7	9.6	1.3	-	3.9

The results show that the ChlorOut tests have a much higher quota S/Cl compared to the reference tests which indicates a better sulphation of the deposits. A higher sulphate flow gives more sulphur in the deposits. There is no clear correlation between temperature and the composition of S and Cl in the deposits.

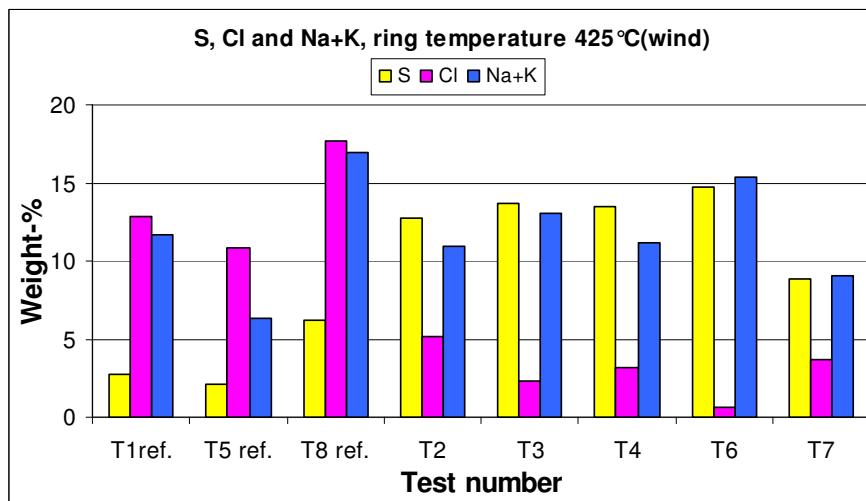


Figure 7, Sulphur (S), chlorine (Cl) and sodium+potassium (Na+K) in deposits from deposit measurements T1-T8 (425 °C, wind)

#### 5.1.4.2 Lee-side

The lee-side deposits (Figure 8) show similar patterns as the wind side. Chlorine decreases and sulphur increases during the ChlorOut tests. A difference from the wind side is that the alkali increases during the ChlorOut test. Test T8 ref. differs from the other reference tests with low chlorine and high sulphur and alkali contents. This cannot be explained. Test T2 also show a different pattern compared

to the ChlorOut tests with very high chlorine content. This indicates that the flow used during T2 was not enough.

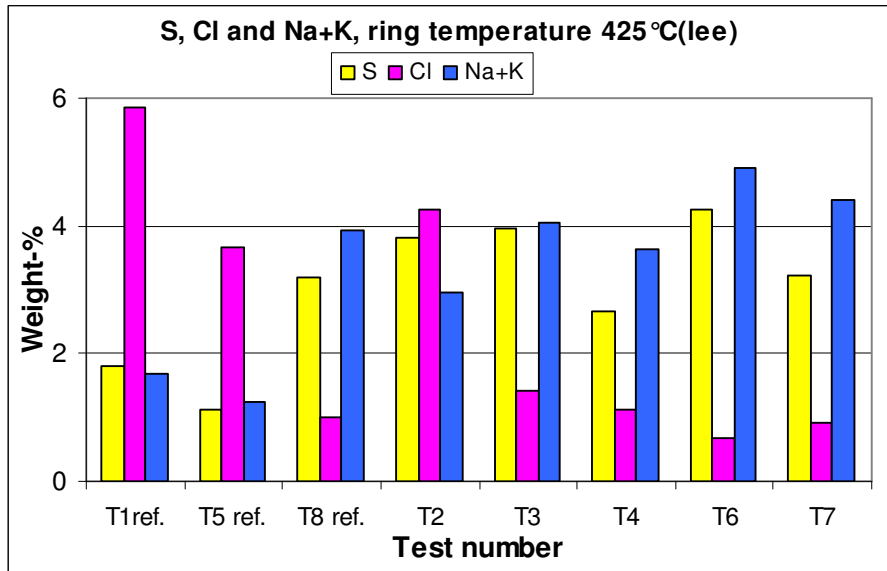


Figure 8, Sulphur(S), chlorine(Cl) and sodium+potassium(Na+K) in deposits from deposit measurements T1-T8 (425 °C, lee)

When comparing the relation S/Cl the patterns are the same as for the wind side with higher values for the ChlorOut tests except for T8 ref., which as mentioned had low chlorine levels compared to the other reference tests.

Table 14, Relation S/Cl from lee side deposits during TP1

	T1 ref.	T5 ref. High O <sub>2</sub>	T8 ref.	T2	T3	T4 High O <sub>2</sub>	T6	T7
Flow [l/h]				25+25	50+50	50+50	50+150	25+50
Dosage point	-	-	-	11&12	10&12	10&12	11&12	11%12
S/Cl								
375°C	0.3	0.2	2.2	0.5	2.5	1.3	3.7	1.1
425°C	0.3	0.3	3.2	0.9	2.8	2.4	6.3	3.5
500°C	0.6	0.2	1.0	0.7	4.0	1.9	12.7	2.7

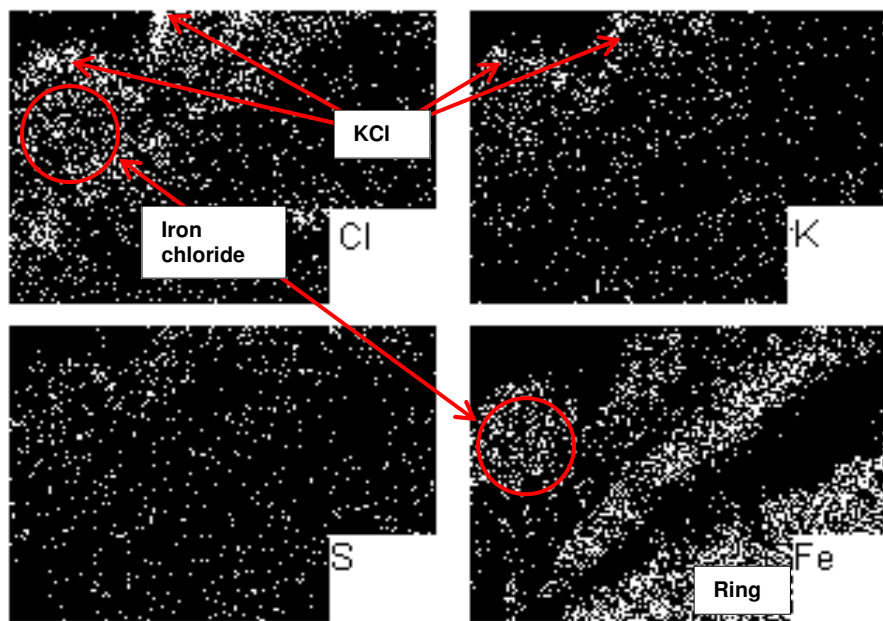
*The elemental analysis show that the Cl level in the deposits can be lowered with dosage of ammonium sulphate to the flue gas. A higher flow gives a better reduction. Sulphur increases in the deposits during all ChlorOut tests. The alkali metals do not show any clear correlation with the ammonium sulphate. The analyses of the lee side deposits are less accurate as they were much thinner than the wind side deposits and did include elements in the deposit-rings.*

#### 5.1.5 Cross-sectional analysis

The cross-sectional analyses were performed with the same SEM/EDX microscope as the elemental analyses. The analyses were performed on all detectable elements on the wind side of the rings. The aim with the cross-sectional analyses was to determine where the different elements were located in the deposit. The complete results from selected rings are presented in Appendix 4 while the presentation in this chapter concentrates on Cl, K, S and Fe.

##### 5.1.5.1 Reference tests

The results from the cross-sectional analyses from reference test T5 is presented below in Picture 12. As can be seen, both potassium and chlorine are present at the same place in the deposit indicating that KCl had condensed directly on the surface of the metal. Chlorine is also present with iron indicating that chlorine had penetrated the iron oxide layer as described by [1] and that corrosion had started already after 3-hours of operation. Almost no sulphur was found in the cross-section.

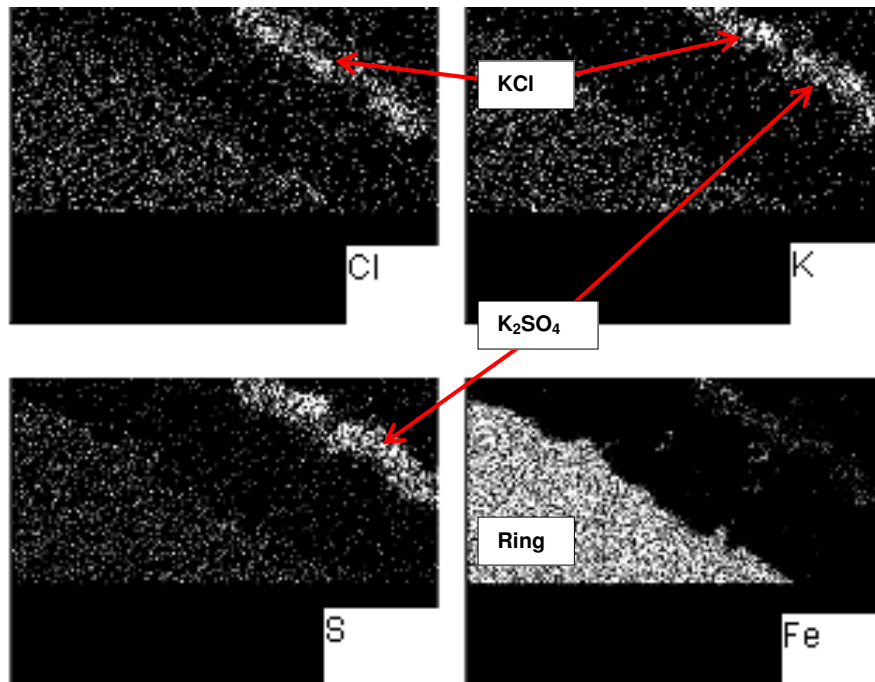


Picture 12, Location of chlorine (Cl), potassium (K), sulphur (S) and Iron (Fe) on ring 14 wind (425°C) from T5 ref. The white dots indicate the element noted on each map.

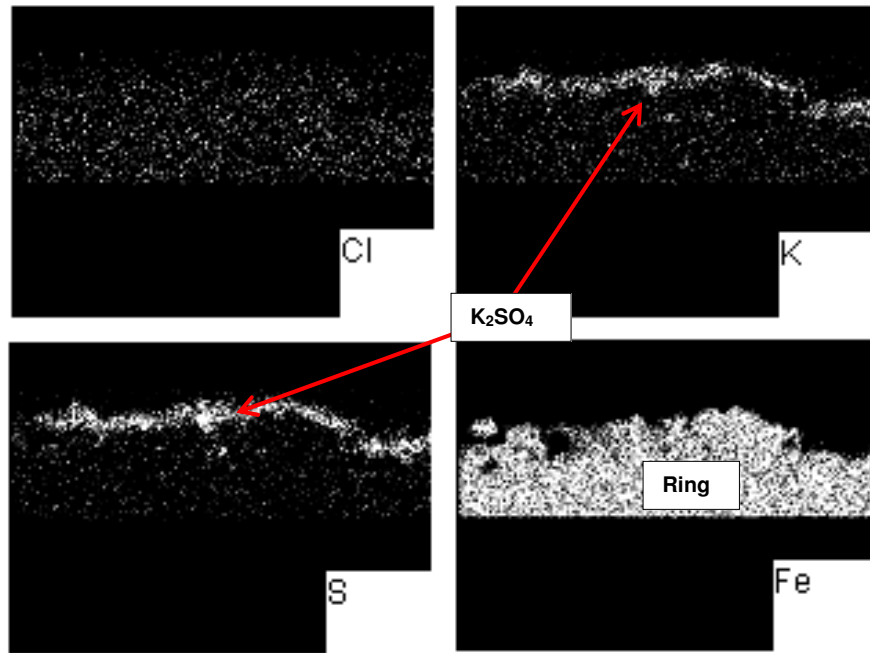
##### 5.1.5.2 ChlorOut tests

The results for Cl, K, S and Fe from analysis of ring 21 (425 °C) from test T7 are presented in Picture 13. Total results are presented in Appendix 4. During ChlorOut test T7 both potassium and chloride were present in the deposit but in contrary to the reference test a higher amount of sulphur was also found in the same region as potassium. This indicates that the deposit partly consisted of potassium sulphate ( $K_2SO_4$ ). Only very small amounts of iron was found outside of the ring indicating that the iron oxide layer was more intact compared to the reference test.

This together indicates that the corrosion rate had decreased due to dosage of ammonium sulphate. This gets even clearer when analysing the cross-section from test T6 in Picture 14. The high flow of ammonium sulphate during T6 has given a thick  $K_2SO_4$  layer directly on the ring surface and no chlorine is found in the deposit. No iron is found outside of the ring.



Picture 13, Location of chlorine, potassium, sulphur and iron on ring 21 wind (425 °C) from ChlorOut test T7. The white dots indicate the element noted on each map.



Picture 14, Location of chlorine, potassium, sulphur and iron on ring 17 wind (425 °C) from ChlorOut test T6. The white dots indicate the element noted on each map.

*The cross-sectional analyses during TP1 show that more sulphur is present in the deposits with potassium during the ChlorOut tests and that less iron has separated from the ring than during the reference tests. This indicates that the corrosion rate was decreased during the dosage of ammonium sulphate to the flue gas.*

## 5.2 Test period 2

### 5.2.1 Operational data

Operational data for TP2 is presented in Table 15 and flue gas measurements in Table 16. A bar chart over the flue gas measurements is presented in Figure 9.

Table 15, Average values on operational data during 6-hour tests.

	T9 ref.	T10 ref.	T11	T12
Flow [l/h], Dosage point	-	-	50+50,11&12	25+50,11&12
Bed temp. [°C]	809	810	810	811
Temp. SH1 [°C]	379	379	378	378
Temp. SH2 [°C]	388	386	387	387
Temp. above cyclone [°C]	819	821	822	818
Temp. before SH2 [°C]	744	745	744	745
Temp. after SH2 [°C]	591	595	591	595
Steam load [kg/s]	22.1	22.5	22.5	22.6
Electrical load [MW]	19.6	20.0	20.0	20.0



Table 16, Average values of SO<sub>2</sub>, CO, NO and O<sub>2</sub> during 6-hour tests

	T9, ref.	T10, ref.	T11	T12
SO <sub>2</sub> [mg/m <sup>3</sup> ]	186	146	290	285
CO [mg/m <sup>3</sup> ]	33	23	35	35
NO [mg/m <sup>3</sup> ]	85	85	44	48
O <sub>2</sub> [%]	4.4	4.3	4.4	4.5

Operating conditions during the tests were normal and no spectacular variations can be seen from the average values in Table 15. The flue gas measurements reveal a clear increase in SO<sub>2</sub> during the ChlorOut tests and a slight increase in CO. NO drops as expected when adding ammonia from 85 mg/m<sup>3</sup> to ~46 mg/m<sup>3</sup>. The higher flow in T11 compared to T12 does not have, from these measurements, any noticeable effect on compounds investigated.

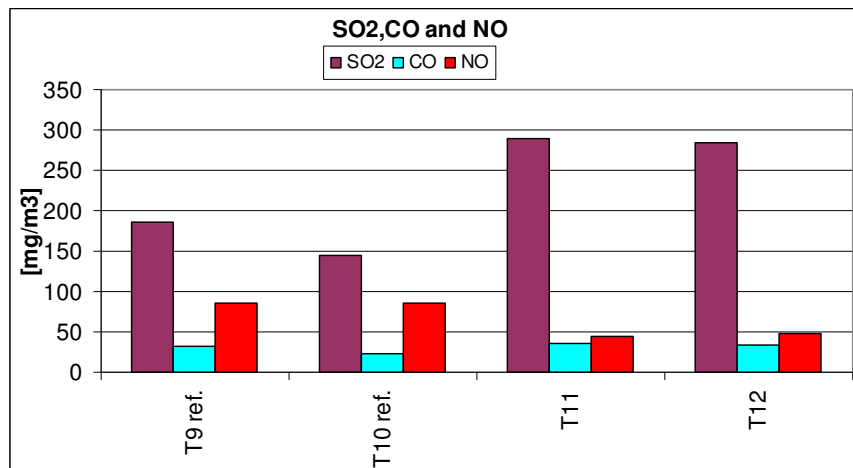


Figure 9, SO<sub>2</sub>, CO and NO during tests in TP2

*The nitrogen oxides decrease during both ChlorOut tests as expected when adding ammonia to the flue gases. The carbon monoxide level has a minor increase during the ChlorOut tests compared to the reference tests. Adding ammonium sulphate to the flue gases increases the SO<sub>2</sub> level out from the super heater region.*

### 5.2.2 IACM

The results from the IACM measurements show the same pattern as during the 3-hour tests with a distinct decrease in KCl (~60 %) and a slight increase in SO<sub>2</sub> during the ChlorOut tests. A slight difference between T11 and T12 can be seen. The higher sulphate flow in T11 seems to have given lower KCl and higher SO<sub>2</sub> levels than in T12 indicating that increased sulphate flows could give better KCl reduction in the flue gas.

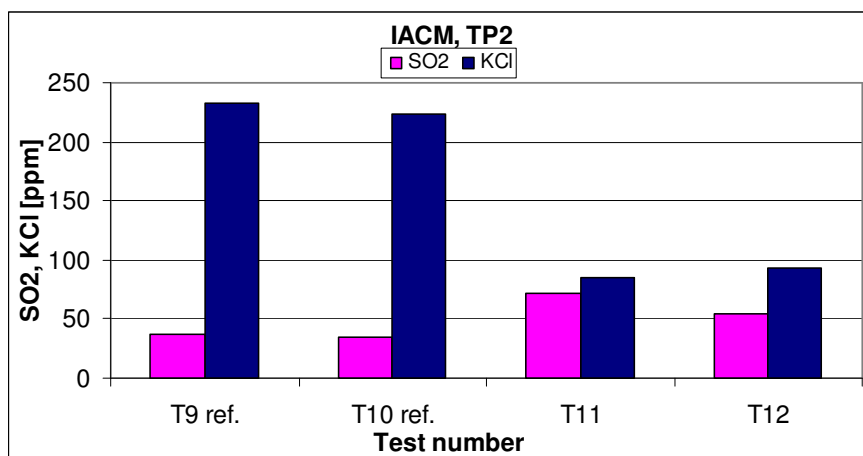


Figure 10, Results from IACM measurements from 6-hour tests.

The KCl response to the sulphate is fast as can be seen in Figure 11. The short disturbances in KCl during the reference tests seem to be related to disturbances in the load.

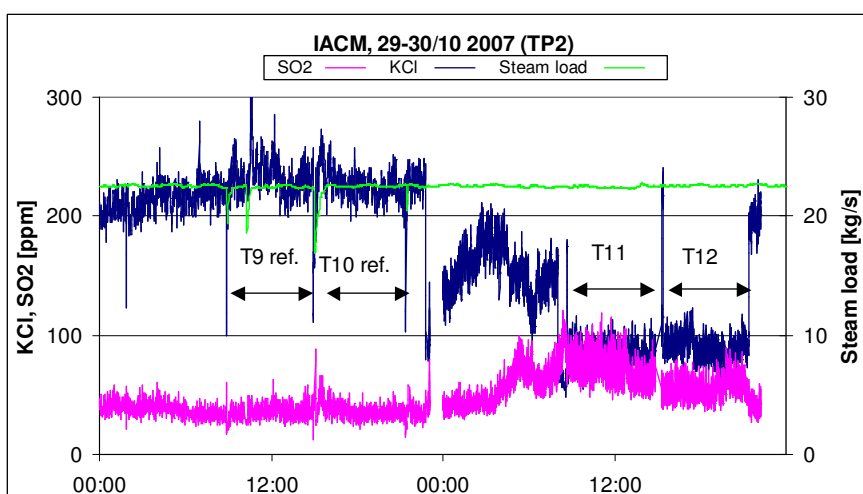


Figure 11, IACM from 6-hour tests, dosage with unknown flow during night before test T11

*The 6-hour tests show similar results as the 3 hour tests. The alkali chloride level decreases radically during the 6-hour ChlorOut tests and SO<sub>2</sub> increases somewhat due to dosage of ammonium sulphate. The alkali chloride response to the ammonium sulphate is instantaneous.*

### 5.2.3 Deposit growth

The results from the 6-hour tests are presented in Table 17 and Figure 12. The big variations within the tests reveal that the soot blowing had a big influence on the

deposits. Alarming is that ring 71 (540°C) from test T12 has lost weight. As the future analyses will depend on the composition of the deposits and as the deposit from, at least test T12, has been severely damage by the soot blowing extra care will be taken when evaluating the test.

Table 17, Deposit growth rate [g/m<sup>2</sup> h], TP2.

	Ring temperature		
Test	425°C	475°C	540°C
T9 ref.	24.1	7.7	26.3
T10 ref.	7.5	7.0	40.7
T11	20.4	12.8	14.8
T12	7.6	14.9	-3.7

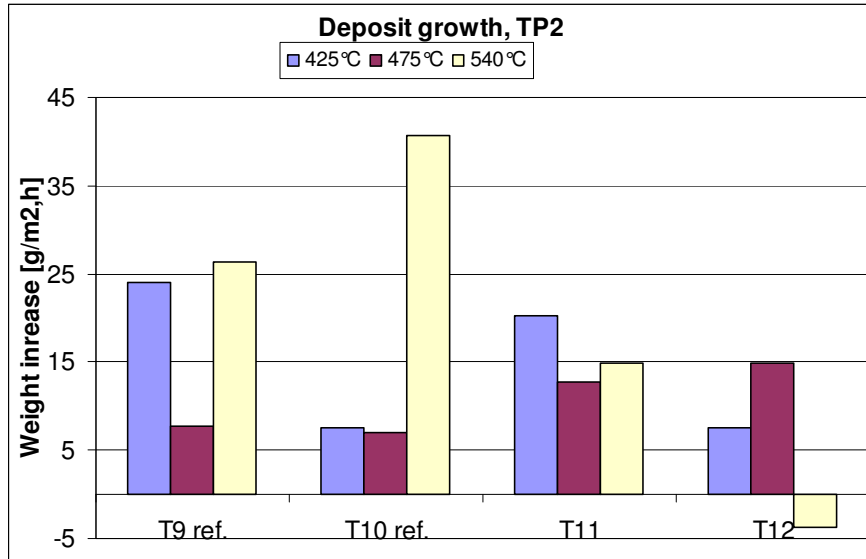


Figure 12, Deposit growth during 6-hour tests, Bergkamen.

*The results from the deposit growth measurements during test period 2 revealed uncertainties around test T12. The test lost weight which was not expected. A probable cause was the soot blowing.*

#### 5.2.4 Elemental analysis

The total elemental analysis of rings from TP2 is presented in Appendix 2. In this chapter the weight will be put on S, Cl and Na+K. Results, in weight %, for wind and lee side are presented in Table 18. Bar charts for wind and lee side are presented in Appendix 3.

Table 18, Cl, S and Na+K in deposits on wind and lee side of rings from TP1. Values in weight -% of the deposit.

		Wind			Lee		
Ring nr.	Test	Cl	S	Na+K	Cl	S	Na+K
	T9 ref.	[Weight -%]					
60	425°C	3.6	7.1	2.5	2.0	6.3	4.5
61	475°C	10.8	6.6	9.7	1.4	7.2	5.4
62	540°C	9.2	5.7	7.6	6.3	2.6	6.7
	T10 ref.						
63	425°C	18.3	6.9	18.7	2.2	3.6	3.2
64	475°C	21.5	6.1	20.0	2.2	6.5	4.5
65	540°C	5.7	6.4	2.7	5.7	4.4	5.1
	T11 50+50 l/h, 11&12						
66	425°C	3.3	13.0	13.3	3.0	4.4	3.6
67	475°C	1.5	14.2	12.1	2.1	5.7	4.1
68	540°C	0.7	9.3	6.1	0.3	7.1	10.2
	T12 25+50 l/h, 11&12						
69	425°C	19.7	5.6	17.3	2.9	3.7	4.1
70	475°C	2.5	12.9	12.7	1.6	4.0	4.8
71	540°C	6.2	9.2	4.6	2.8	4.2	3.6

The figures reveal uncertainties around the two reference tests as they differ in composition and pattern. When comparing the tests with the 3-hour reference tests, test T9 ref. clearly deviates from the other references (Figure 13). T12 also deviates from expected values as can be seen in Figure 14. This could all be related to the soot blowing and as T12 showed uncertainties in the deposit growth measurements both T9 ref. and T12 will here after be excluded from further evaluation. All 6-hour lee side measurement will as well no longer be handled to exclude uncertainties around the measurements. This leaves test T10 ref. (wind) and test T11 (wind) for evaluation.

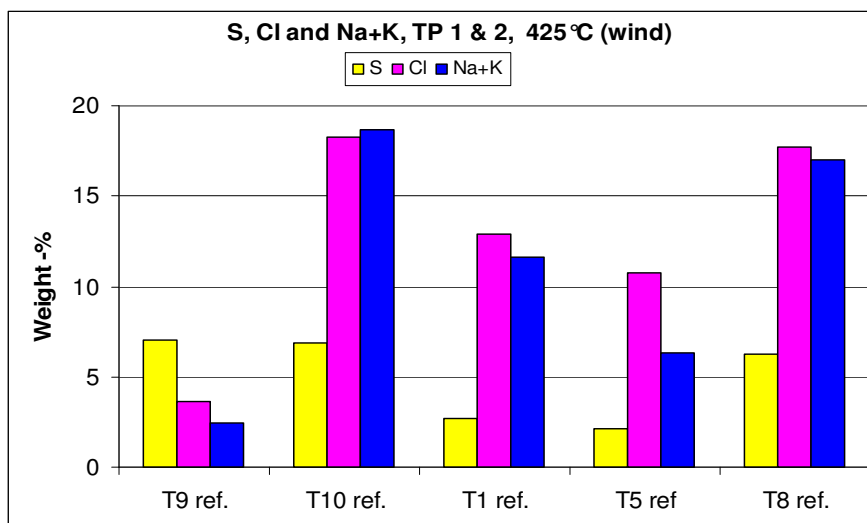


Figure 13, Comparison between reference tests from TP1 and TP2

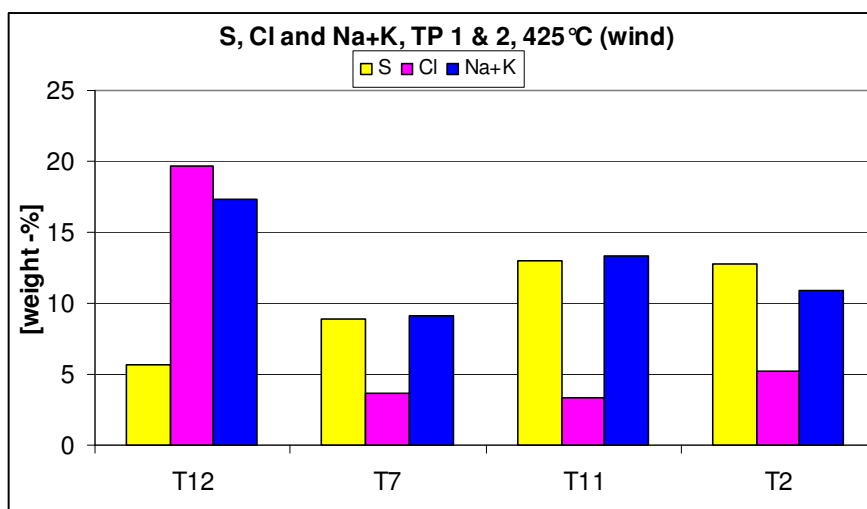


Figure 14, Test T12 compared to similar tests from TP 1&2

Results for T10 ref. and T11 show that chlorine has decreased and sulphur has increased in the deposit during ChlorOut test T11 compared to T10 ref. The trend for T10 ref. at 540°C deviates from the other temperatures that cannot be explained except that the soot blowing might have disturbed the test.

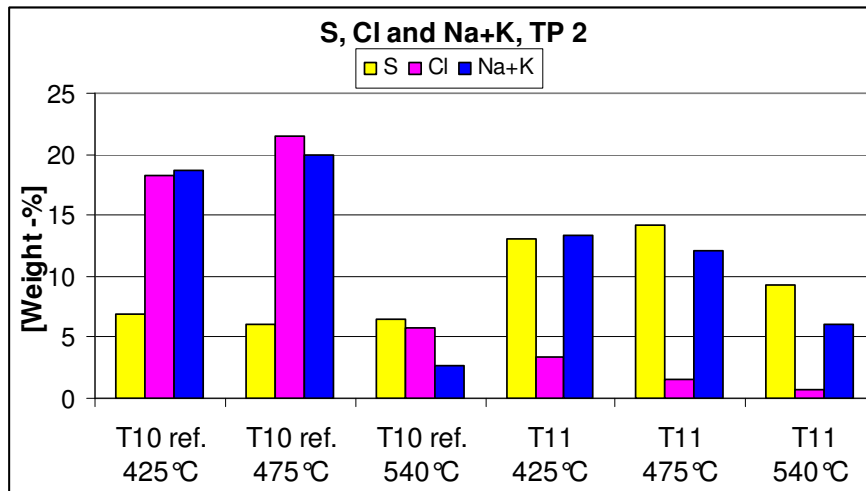


Figure 15, S, Cl and Na+K from TP2

*From the results, deposit test T9 ref. and T12 were excluded from further evaluation due to uncertainties around the soot blowing. The 6-hour tests show the same trends as the 3-hour tests with decreasing Cl and increasing S in the deposits during dosage of ammonium sulphate.*

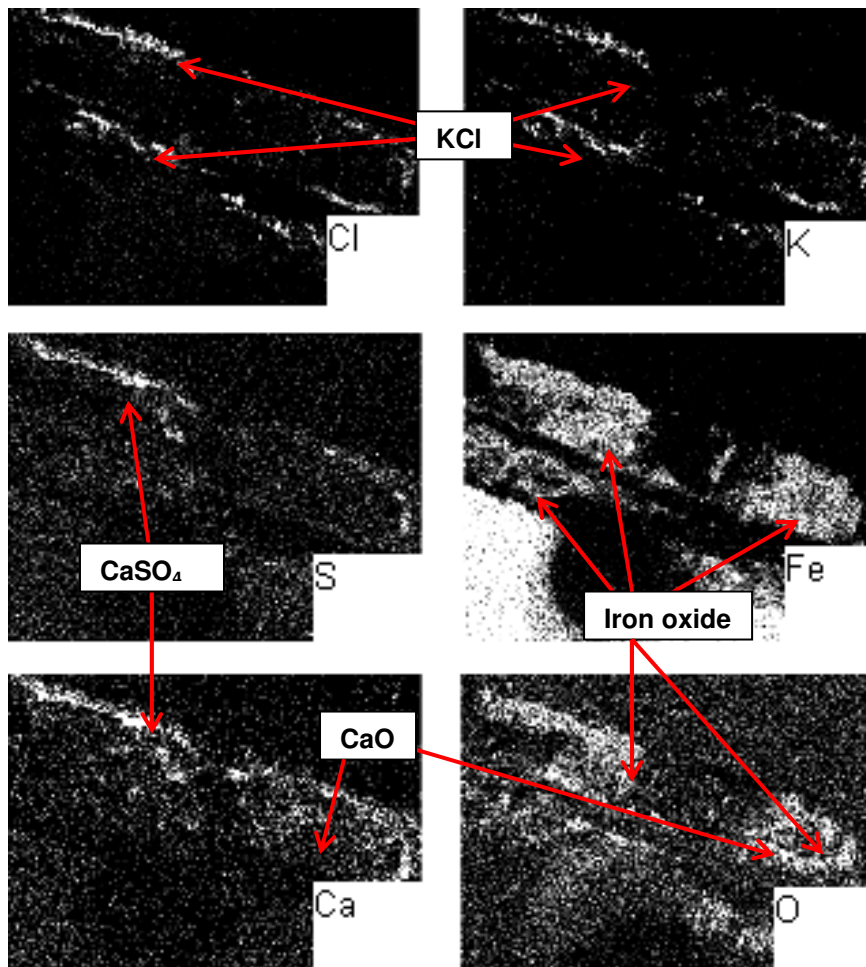
### 5.2.5 Cross-sectional analysis

Cross-sectional analyses were performed on the wind side of selected rings. The results are presented separately for reference tests and ChlorOut tests. Besides K, S, Cl and Fe was also Ca found in big quantities in the cross-section and will therefore also be evaluated.

#### 5.2.5.1 Reference tests

As during TP1 the chlorine seems to have penetrated the protective iron oxide layer (Picture 15) described in chapter 3.3. Chlorine is found in relation to potassium above and under a thick iron oxide layer, which has separated from the ring. Sulphur is also found but in smaller quantities than chlorine in relation to both potassium and calcium indicating that either or both  $K_2SO_4$  or  $CaSO_4$  (calcium sulphate) has stuck on the ring. Calcium is also present with oxygen as CaO (calcium oxide).

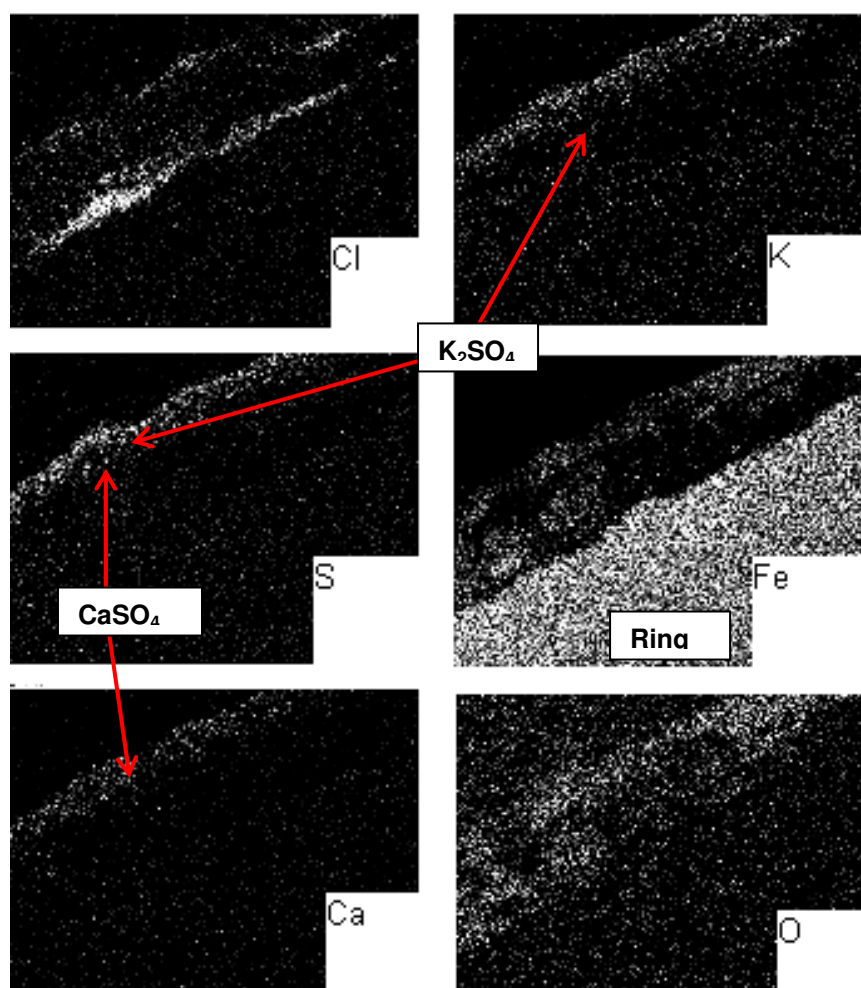
These observations show that corrosion had started in the boiler after 6 hours of normal operating conditions (no flow and same metal in the ring as SH 2).



Picture 15, Location of chlorine, potassium, sulphur, iron, calcium and oxygen on ring 63 wind (425 °C) from T10 ref. The white dots indicate the element noted on each map.

#### 5.2.5.2 ChlorOut tests

Picture 16 shows the relation between the different elements in the cross-section of ring 66 from test T11. The analysis reveals increased amounts of sulphur in the cross-section compared to the reference tests. The sulphur is mainly present as  $K_2SO_4$  or  $CaSO_4$  in the periphery of the deposit. Chlorine was found in the whole cross-section indicating that it had penetrated the iron oxide layer. In difference to the reference tests less chlorine had deposited on the ring and the iron oxide layer was much thinner. More sulphur was found and in a clearer relation to potassium indicating more  $K_2SO_4$  present in the deposit. Calcium is found in relation to sulphur.



Picture 16, Location of chlorine, potassium, sulphur, iron, calcium and oxygen on ring 66 wind (425 °C) from T11. The white dots indicate the element noted on each map

*The observations from the cross-sectional analyses shows that corrosion decreased during the 6-hour ChlorOut tests compared to the reference tests. This is based on that less iron had separated from the ring and that more sulphur was found in the deposit.*



## 6 Discussion

In this chapter follows a discussion of the results presented in chapter 5.

### 6.1 Effect of ChlorOut

Adding of ammonium sulphate to the flue gases in the Bergkamen boiler clearly reduces the amount of KCl in the flue gas. The sulphate also affects the composition of deposits in the super heater region. In all tests performed the chlorine level decreases and the sulphur content increases in the deposit. Table 19 shows the rate of reduction for KCl and Cl (425 °C) during the ChlorOut tests from TP1. During dosage of ammonium sulphate KCl is reduced by 20-80 % and the chlorine deposited on the deposit probe is reduced by 60-95 %. Sulphur increases radically in the deposits during all tests.

Table 19, Reduction of KCl (in flue gas) and Cl (in deposit, 425°C) expressed as percentage during ChlorOut tests. References are calculated from average values of the reference tests from each test period.

Test number	T2	T3	T4 High O <sub>2</sub>	T6	T7	Tref. Avg.
Flow [l/h], Dosage point	25+25, 11&12	50+50, 10&12	50+50, 10&12	50+150, 11&12	25+50 11&12	-
KCl reduction	22 %	60 %	64 %	79 %	73 %	214.7 ppm
Cl reduction (425 °C)	62 %	83 %	77 %	95 %	74 %	13.8 weigh -%
S increase (425°C)	348 %	372 %	368 %	402 %	241 %	3.7 weigh -%

The effect of the reduced KCl in the flue gas on the chlorine content in the deposits is presented in Figure 16. The figure show a clear correlation between KCl and Cl. Reduction of KCl in the flue gas reduces Cl in the deposits. The effect of the chlorine decrease will be discussed later on in this report. In Figure 17 is sulphur added to visualize how the ammonium sulphate also affects the S content in the deposits. Sulphur clearly increases in the deposits when adding ammonium sulphate to the flue gas.

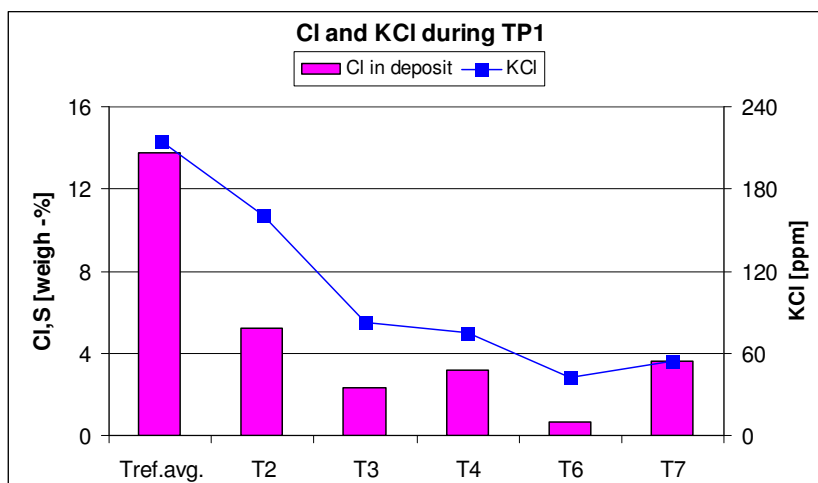


Figure 16, Effect of reduced KCl in the flue gas on the Cl content in deposits

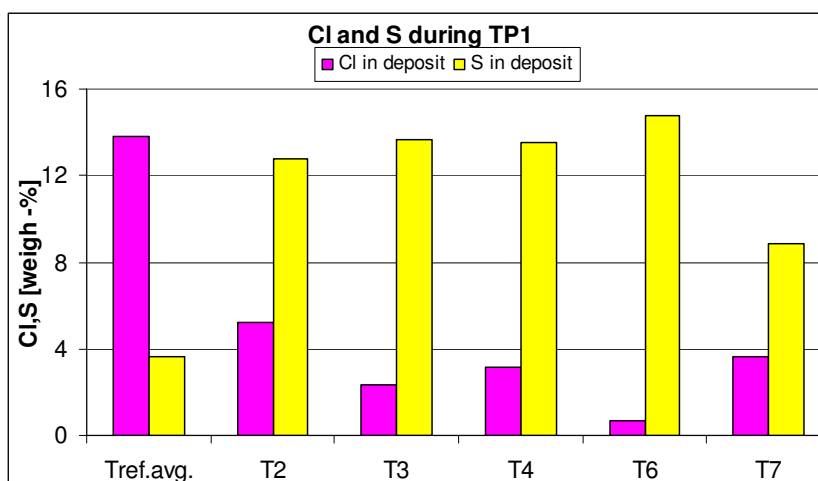


Figure 17, Chlorine and sulphur in deposits (425°) during TP1

### 6.1.1 Corrosion

It is not possible from the deposit and IACM measurements performed in Bergkamen to determine the rate of corrosion in the boiler. If compared to tests performed in other boilers it is though possible to decide the trend for the corrosion. In two Swedish boilers, Munksund CFB [7] and Idöbäcken BFB, have corrosion measurements been performed in ChlorOut installations. Both boilers show a clear reduction of KCl in the flue gas and Cl in the deposits. Both corrosion measurements also show a clear trend. The reduced chlorine content in the deposits, as a result of the reduced KCl level in the flue gas, reduced the corrosion rate in the boilers by 70 % and 50 %.

The reduction in the Bergkamen boiler is for KCl ~20-80 % and for the chlorine in the deposit ~60-95 %. If comparing these results with the results from the two

boilers mentioned, a reduced corrosion rate in the Bergkamen boiler is very probable.

Table 20, Comparison in KCl-, Cl- and corrosion reduction due to dosage of ammonium sulphate.

Boiler	KCl reduction	Cl reduction	Reduced corrosion rate
Bergkamen	20-80 %	60-95 %	Not known
Munksund	90 %	100 %	70 %
Ildbäcken	47 %	100 %	50 %

Even though a reduction is very probable the actual rate of corrosion is not known. In Bergkamen the chlorine reduction in the deposits is from 10-20 weight-% of the deposit to about 1-4 weight-% of the deposit. The chlorine in both Ildbäcken and Munksund was almost totally reduced and it is not known how high the corrosion rate will be due to the chlorine left in the Bergkamen deposits. A reduction from the present corrosion rate is though very probable.

### 6.1.2 Nitrogen oxide, NO

NO is reduced in all ChlorOut tests performed and the reduction rate is shown in Table 21. The reduction is due to the NH<sub>3</sub> added with the ammonium sulphate and increases with the ammonia flow. The higher NO level in test T4 compared to test T3 is due to the higher oxygen level as described in chapter 3.5.

Table 21, Reduction of NO during ChlorOut tests

	T2	T3	T4 High O <sub>2</sub>	T6	T7	Tref.avg.
Flow [l/h]	25+25	50+50	50+50	50+150	25+50	-
Dosage point	11&12	10&12	10&12	11&12	11&12	
Reduction of NO	35%	67%	46%	71%	40%	97.8 mg/m <sup>3</sup>

### 6.1.3 Carbon monoxide, CO

The behaviour of CO is of interest as it varies between different installation sites. In Bergkamen the trend was a slight increase of CO during ChlorOut tests but in other installations the trend has been the opposite and as chapter 3.6 reveals is the chemistry behind CO not very simple. Important is the OH radical pool that controls the oxidation of CO. Anything that competes for the radicals will cause an increase in CO. What exactly disturbs the CO chemistry in Bergkamen is hard to predict. SO<sub>2</sub> increases in some of the ChlorOut tests and as mentioned in chapter 3.6 has SO<sub>2</sub> shown to have an inhibiting effect on the CO oxidation. NO decreases which according to [15] could inhibit the CO oxidation while HCl has both shown to enhance and inhibit the oxidation.

When studying the curves for NO and CO in Figure 18 and Figure 19, CO fluctuates more when adding sulphate in position 10 than in position 11. The fluctuations are decreased when increasing the oxygen level.

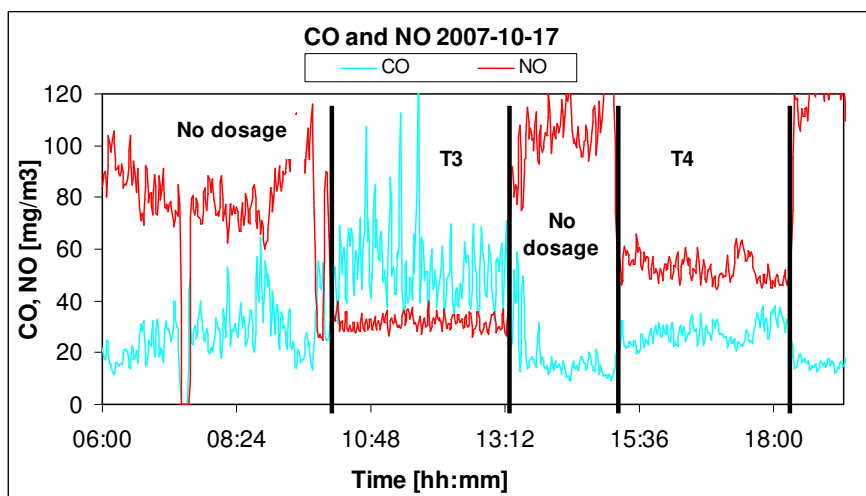


Figure 18, CO and NO during deposit measurements T3 and T4.

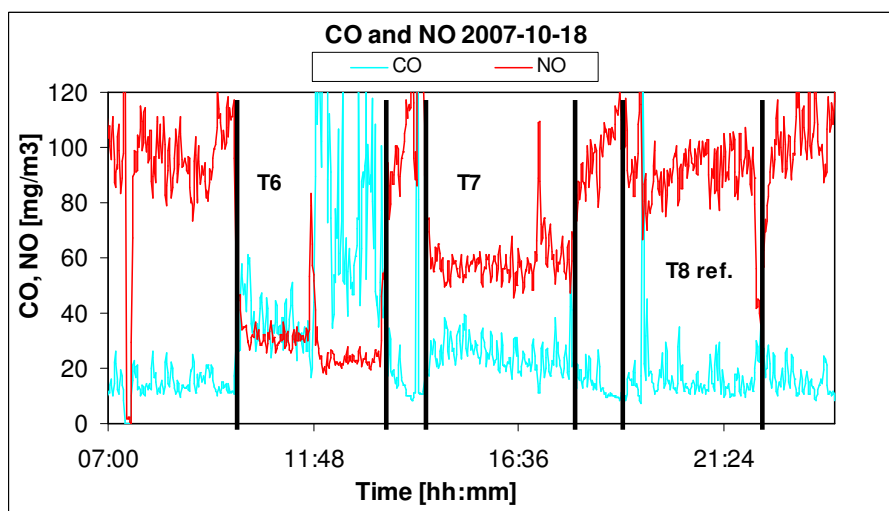


Figure 19, CO and NO during deposit measurements T6, T7 and T8 ref. The sudden increase in CO during T6 could be a cause of the broken flow meter.

During test T6 a sudden increase in CO appears in the middle of the test period together with a slight decrease in NO. This event could have been caused by the failure in the flow meter, which yielded higher flows of ammonium sulphate than expected. Ammonia competes for the OH radical pool as shown in reaction R12.

#### 6.1.4 Deposit growth

The effect of ammonium sulphate on the deposit growth rate is shown in Figure 20. The trend is a reduced growth rate with increased sulphate flow. The clearest trend is at 500°C where the reduction is >100 % for all ChlorOut tests. The deposit growth rate during test T2, except for ring 6 (500°C), is similar as during the reference tests indicating that, for the present steam temperature, a flow of 25+25 is too small

to get any change in the deposit growth. The least growth is found in T6 where the highest sulphate flow was used.

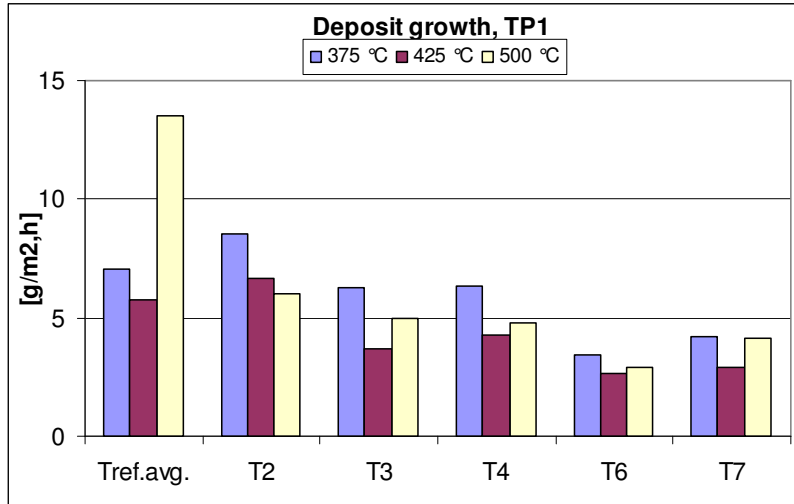


Figure 20, Deposit growth during TP1

#### 6.1.5 Influence of oxygen

The effect of O<sub>2</sub> on the reduction of KCl and “Cl in the deposit” in the flue gas is presented in Figure 21. The figure shows no clear relation between oxygen level and KCl and Cl. The slightly lower Cl during normal conditions is not enough to draw any conclusions.

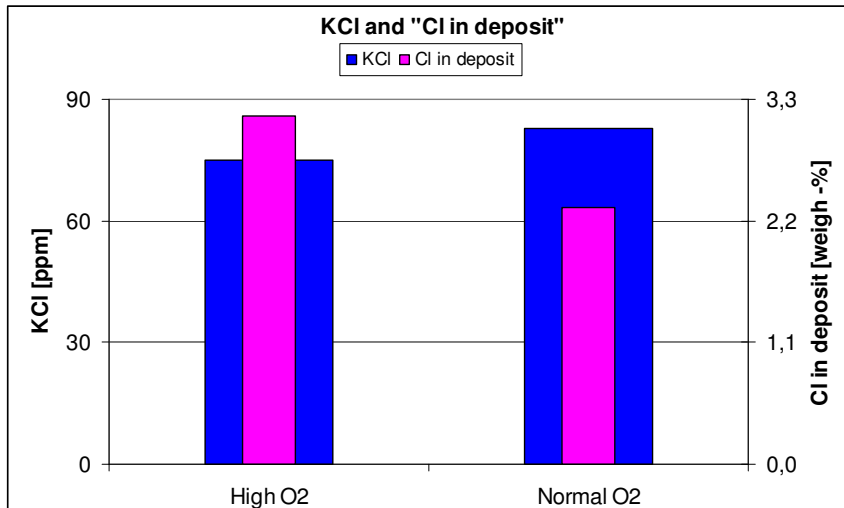


Figure 21, Reduction of KCl and Cl during different oxygen conditions

The effect of the increased oxygen level on SO<sub>2</sub> (IACM), CO and NO is presented in a bar chart in Figure 22. An increased oxygen level clearly reduces CO as

described in chapter 3.6.  $\text{SO}_2$  also decreases indicating an increased activity of reaction R10. NO increases with oxygen level as mentioned in chapter 3.5.

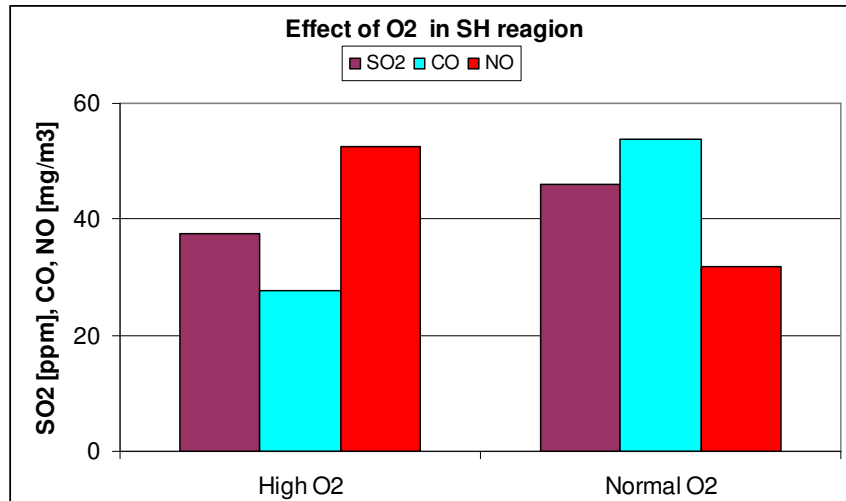


Figure 22, Effect of oxygen on  $\text{SO}_2$ , CO and NO in SH region. High O<sub>2</sub>=T4 and Normal O<sub>2</sub>=T3.

The oxygen dependence on the deposit growth is shown in Figure 23 and from these tests there seems to be no correlation between deposit growth and oxygen level in the boiler.

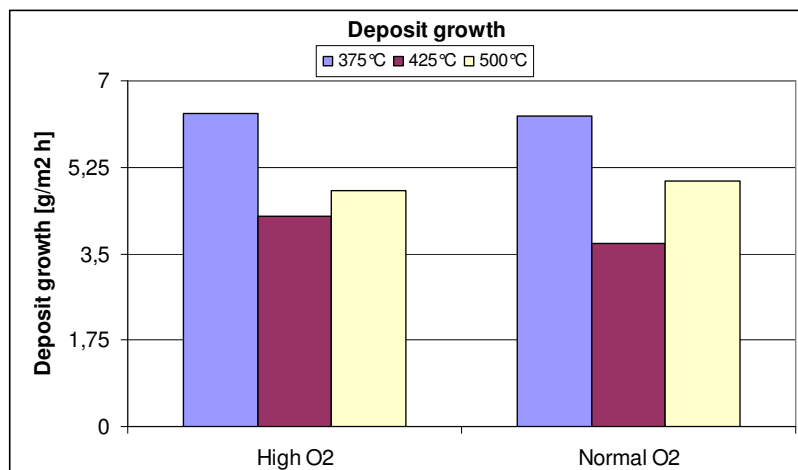


Figure 23, Temperature dependence on deposit growth; High O<sub>2</sub>=T4, Normal O<sub>2</sub>=T3

## 6.2 Relation $\text{SO}_2/\text{KCl}$

Ways of predicting the effect of a certain ammonium sulphate flow into a boiler is valuable in order to fast decide an effective flow. Today the flow is controlled on the KCl level in the boiler but this excludes the direct sulphation of KCl in the deposit described in chapter 3.2.3. To also include the solid phase sulphation of KCl the quota  $\text{SO}_2/\text{KCl}$  (IACM) is introduced. By comparing the quota with the chlorine content in the deposits a relation can be established which then probably could be used to predict the chlorine content in the deposits. The quota is unique for every boiler as it depends on the boiler construction that gives specific times for reaction between sulphate and flue gas, specific flue gas strakes, etc. The relation for the Bergkamen boiler is presented in Table 22 and in Figure 24.

Table 22, Relation  $\text{SO}_2/\text{KCl}$  and Cl in deposit for tests during TP 1 & 2

Test number	Flow, Dosage point	$\text{SO}_2$ [ppm]	KCl [ppm]	$\text{SO}_2/\text{KCl}$	Cl in deposit
T1 ref.	-	29.2	219.7	0.1	12.9
T5 ref.	-	23.4	226.8	0.1	10.8
T8 ref.	-	36.1	170.8	0.2	17.7
T10 ref.	-	35.2	223.7	0.2	18.3
T2	25+25 l/h, 11&12	40.4	160.5	0.3	5.2
T3	50+50 l/h, 10&12	46.0	82.8	0.6	2.3
T4	50+50 l/h, 10&12	37.5	74.9	0.5	3.2
T6	50+150 l/h, 11&12	61.3	42.4	1.4	0.7
T7	25+50 l/h, 11&12	45.1	54.8	0.8	3.7
T11	50+50 l/h, 11&12	71.4	85.5	0.8	3.3

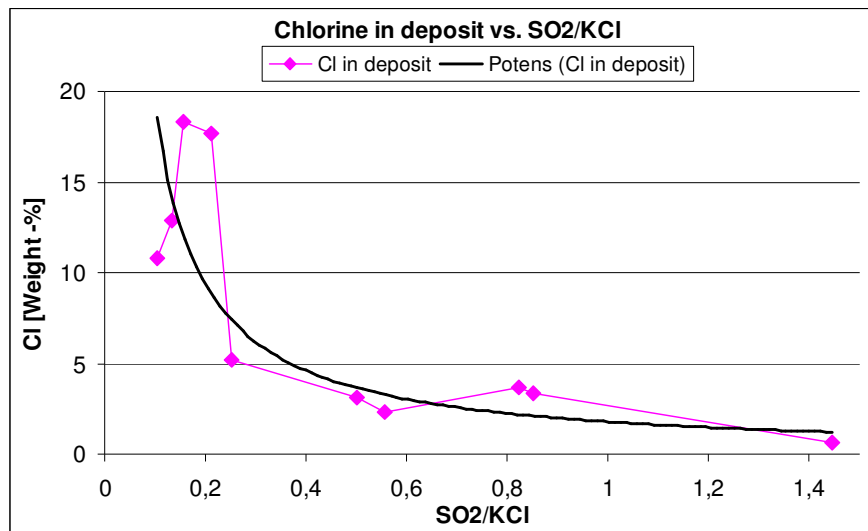


Figure 24, Relation between chlorine in deposit of deposit rings at 425°C and  $\text{SO}_2/\text{KCl}$ .

The results show that a quota  $\text{SO}_2/\text{KCl} > 0.4$  in this case is a good guideline to a low chlorine content in the deposit. Noteworthy is that the quota for test T3 and T4

are lower than for example T7 even though a higher ammonium sulphate flow was used in T3 and T4. A high quota could then mean that there are excess SO<sub>2</sub> that will pass the system without sulphating any chlorides. To estimate where the breakpoint for further dosing ends the chlorine content in the deposit and the SO<sub>2</sub> out from the super heater region is plotted versus the quota SO<sub>2</sub>/KCl as in Figure 25. The results show that the high flow in T6 yielded high excess SO<sub>2</sub> out from the super heater region. Even test T7 gave high excess SO<sub>2</sub> compared to T3 and T4 indicating that position 10&12 is better in reducing SO<sub>2</sub>. A good estimation for the Bergkamen boiler should be a quota somewhere between 0.4 and 0.6.

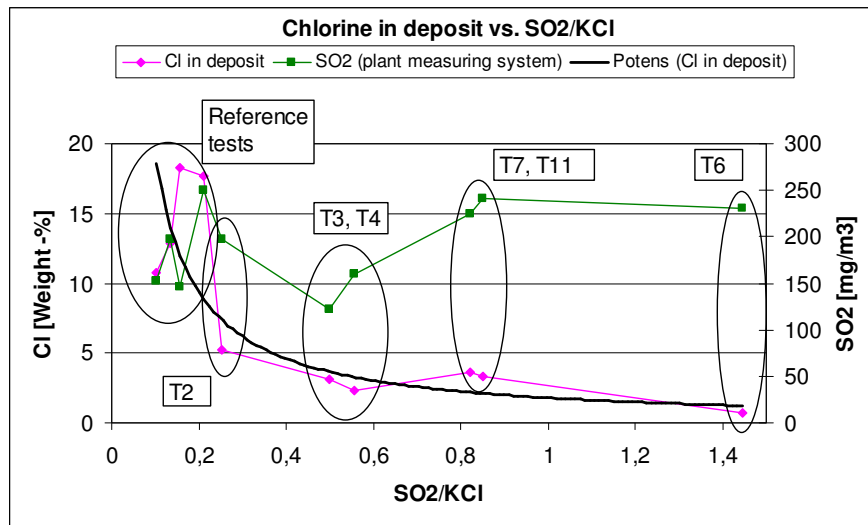


Figure 25, Chlorine in deposit and SO<sub>2</sub> (plant system) plotted on SO<sub>2</sub>/KCl.

### 6.3 Dosage point

The results presented are guiding when trying to choose dosage point. Table 23 shows a comparison between dosage point 10&12 and 11&12. Test T3 and T4 represents dosage point 10&12 and test T2, T6 and T7 represents dosage point 11&12, Figure 26 visualizes the data.

Table 23, Comparison between dosage point 10&12 and 11&12.

	T3	T4 High O <sub>2</sub>	T2	T6	T7	Tref.avg.
Flow [l/h]	50+50	50+50	25+25	50+150	25+50	-
Dosage point	10&12	10&12	11&12	11&12	11&12	-
SO <sub>2</sub> /KCl	0.6	0.5	0.3	1.4	0.8	0.2
Cl in deposit	2.3	3.2	5.2	0.7	3.7	13.8
SO <sub>2</sub> [mg/m <sup>3</sup> ]	160	122	197	230	225	186
KCl[ppm]	83	75	161	42	55	215
NO[mg/m <sup>3</sup> ]	32	53	63	28	58	98
CO[mg/m <sup>3</sup> ]	54	28	44	60	25	21



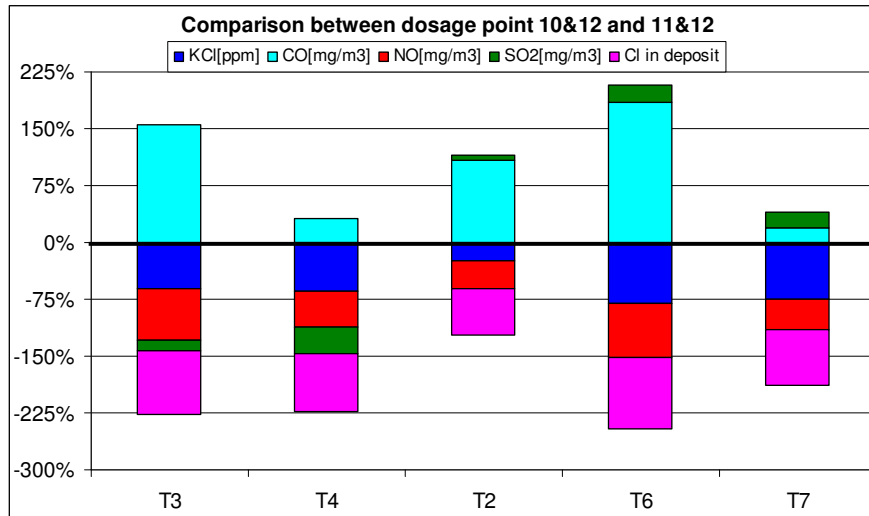


Figure 26, Increase/decrease [%] of compounds in the flue gas during ChlorOut tests compared to average of reference tests.

The clearest trend is that for  $\text{SO}_2$  out from the super heater region as it increases, compared to the reference tests, in all cases except when dosing in 10&12 where  $\text{SO}_2$  decreases. The chlorine decrease is similar between the dosage points. The CO increase is higher when dosing in position 10&12 during normal oxygen conditions. When the oxygen level is increased as in T4 the CO increase stops at a similar value as in T7. Increased oxygen level also mean a more oxidizing condition which, according to [10], is positive when trying to prevent corrosion during combustion of waste wood. Reduction of NO is equal between the dosage points.

From the observations above, and the information that was given in Figure 25, positions 10&12 seems to be a good choice because of the high Cl reduction and the low  $\text{SO}_2$  and not too high CO out from the super heater region.

## 7 Conclusions

The aim with this thesis work was to measure and reduce the alkali chloride level, mainly potassium chloride (KCl), in the flue gases from burning waste wood in a CFB boiler in Bergkamen, Germany. The effects of the reduced KCl level in the boiler on the super heater deposits were then investigated. Measurements of the alkali chloride level were performed with the IACM (In situ Alkali Chloride Monitor) instrument developed by Vattenfall Research and Development AB. Reduction of KCl in the flue gases was achieved by adding ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , to the flue gases before the super heaters. The effect of the change in composition of the deposits on the super heaters was evaluated from a corrosion point of view. Conclusions from the work are:

- It was possible to measure the KCl level in the Bergkamen boiler with the IACM instrument.
- Adding  $(\text{NH}_4)_2\text{SO}_4$  to the flue gases in the CFB in Bergkamen decreased the KCl level in the flue gases.
- The work shows that it is possible, with the ChlorOut concept, to measure and reduce KCl in boilers with very high levels of KCl in the flue gas.
- The deposit measurements showed that the reduction of alkali chlorides in the super heater region reduced the chlorine and increased the sulphur deposited on the super heaters.
- The reduced chlorine content in the deposits will most likely decrease the chlorine-induced corrosion experienced in the boiler.
- Cross-sectional analyses showed that less iron separated from the deposit rings and that less chlorine and more sulphur was present in the deposits during dosage of  $(\text{NH}_4)_2\text{SO}_4$ .
- A reduction in deposit growth was achieved during dosage of ammonium sulphate. The effect was clearest at 500°C.
- NO was reduced and a minor increase in CO could be seen during dosage of ammonium sulphate.

Besides evaluating the chemical effects of ammonium sulphate I have also, in this work, introduced the quota  $\text{SO}_2/\text{KCl}$  in gas phase as a reference for the chlorine deposited on the super heaters. I have also showed that a quota 0.4-0.6 is suitable for a low chlorine content in the deposits and a  $\text{SO}_2$ -low flue gas out from the super heater region in the Bergkamen boiler. The quota is boiler specific and could be used to control the flow of ammonium sulphate to the boiler.

## **8 Acknowledgments**

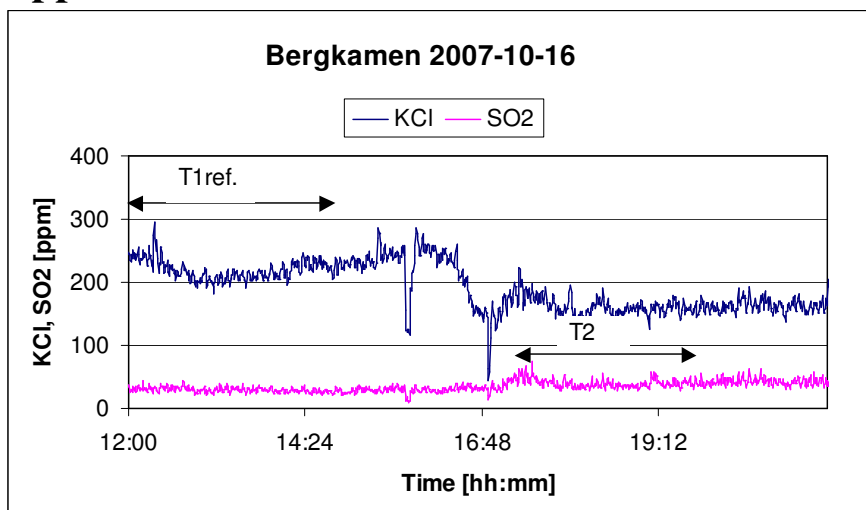
I would like to thank the boiler staff in Bergkamen and especially Stephan Kalbertod for letting me perform the measurements and also Harri Vilokki from Foster Wheeler for providing me with operational data and lunch. The staff at VPC Nyköping also deserve acknowledgment for guiding me and for answering questions when needed. A special thanks to my supervisor Håkan Kassman for guiding me in the jungle of consulting and report writing and Anders Hjörnhede for technical support.

## 9 References

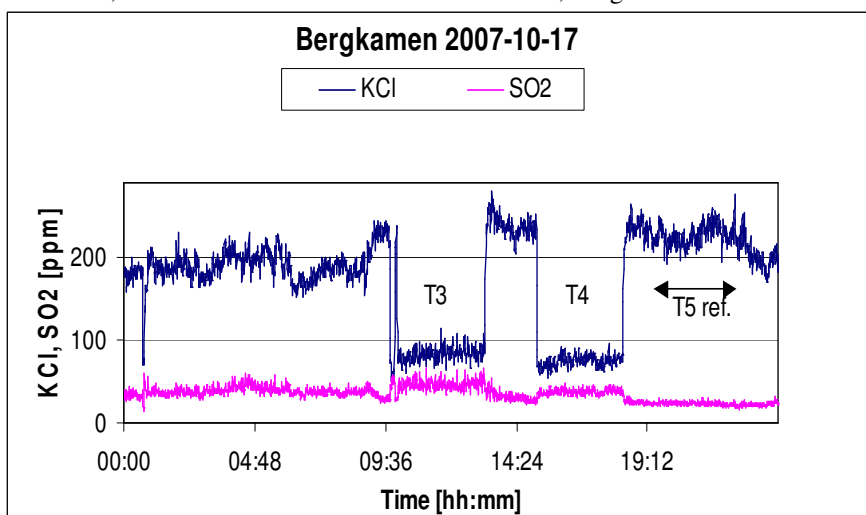
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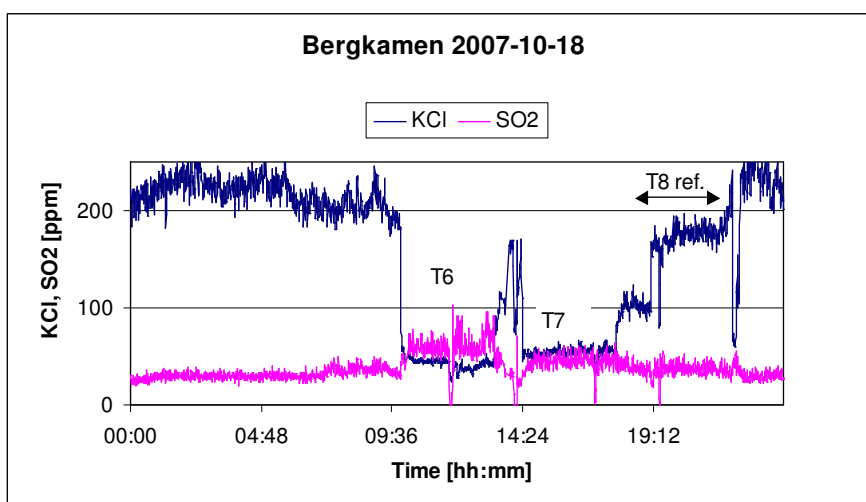
## Appendix 1



Picture 17, KCl and SO<sub>2</sub> from IACM measurements, Bergkamen 2007-10-16



Picture 18, KCl and SO<sub>2</sub> from IACM measurements, Bergkamen 2007-10-17



Picture 19, KCl and SO<sub>2</sub> from IACM measurements, Bergkamen 2007-10-18

## Appendix 2

Appendix 2 contains a total elemental analysis from both TP1 and TP2. Table A2 show the ring number connected to each test.

Table A2, Ring numbers and tests

Ring nr.	Test	Ring temp		Ring nr.	Test	Ring temp
	T1 ref				T9 ref	
1		375°C		60		425°C
2		425°C		61		475°C
3		500°C		62		540°C
	T2				T10 ref	
4		375°C		63		425°C
5		425°C		64		475°C
6		500°C		65		540°C
	T3				T11	
7		375°C		66		425°C
8		425°C		67		475°C
9		500°C		68		540°C
	T4				T12	
10		375°C		69		425°C
11		425°C		70		475°C
12		500°C		71		540°C
	T5 ref.					
13		375°C				
14		425°C				
15		500°C				
	T6					
16		375°C				
17		425°C				
19		500°C				
	T7					
20		375°C				
21		425°C				
22		500°C				
	T8 ref.					
23		375°C				
24		425°C				
25		500°C				











## Appendix 3

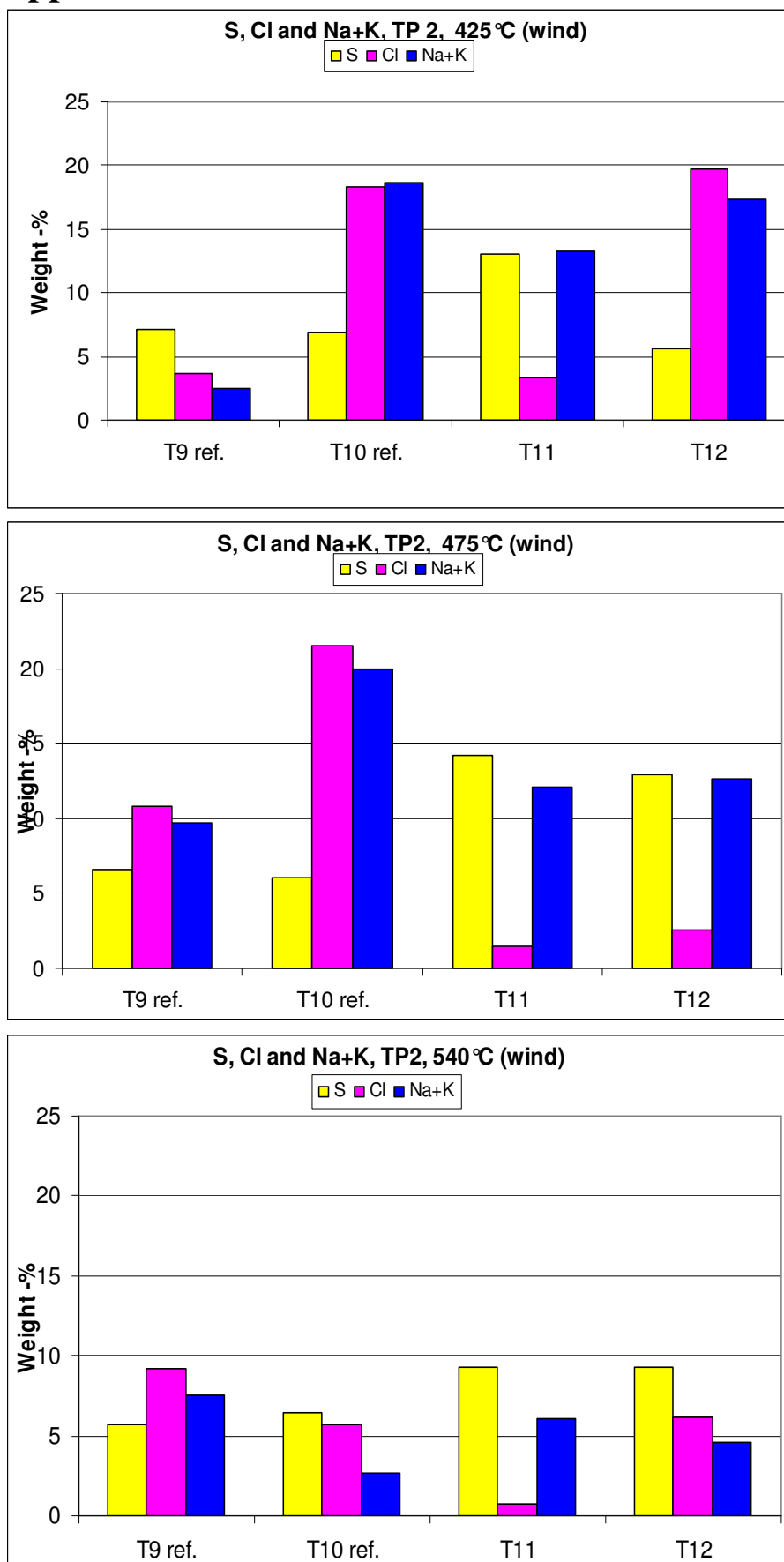


Figure 27, Sulphur, Chlorine and sodium+ potassium in deposits on wind side of deposit rings used during 6-hour tests, Bergkamen

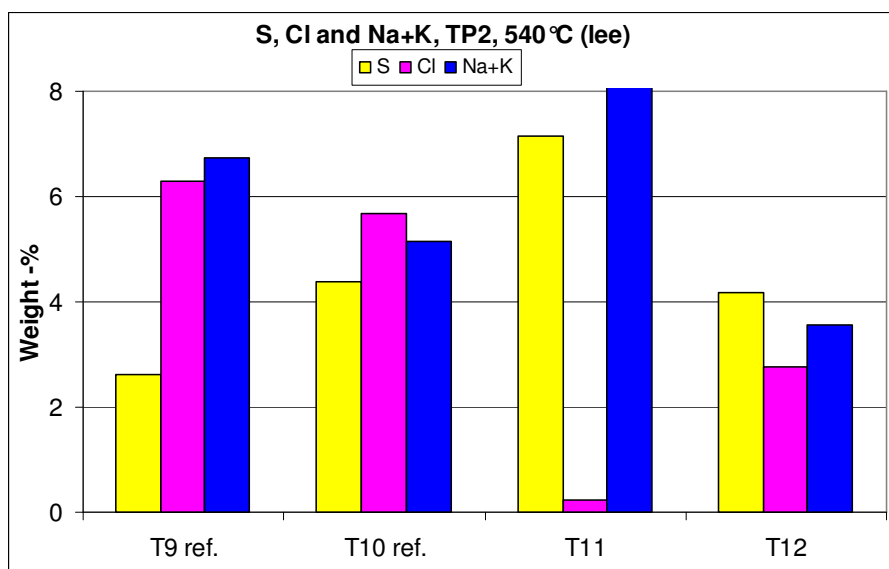
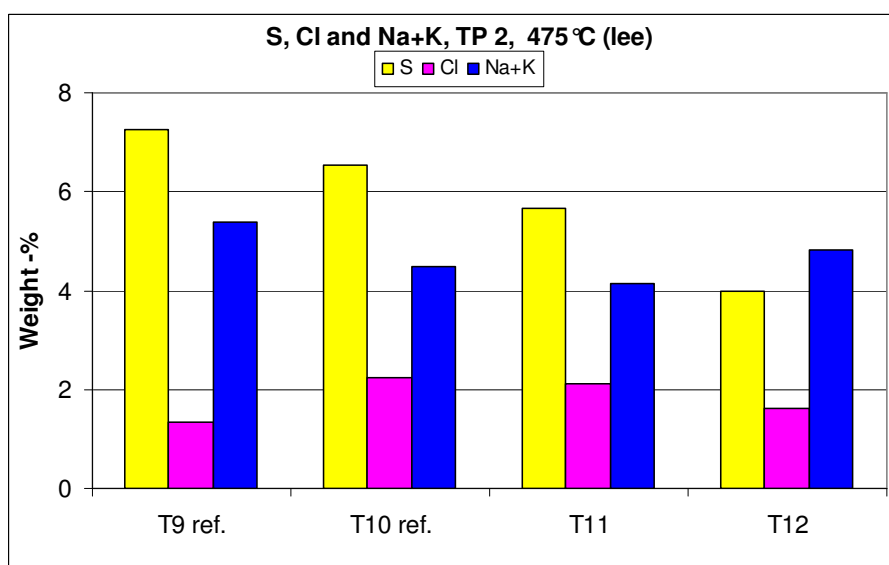
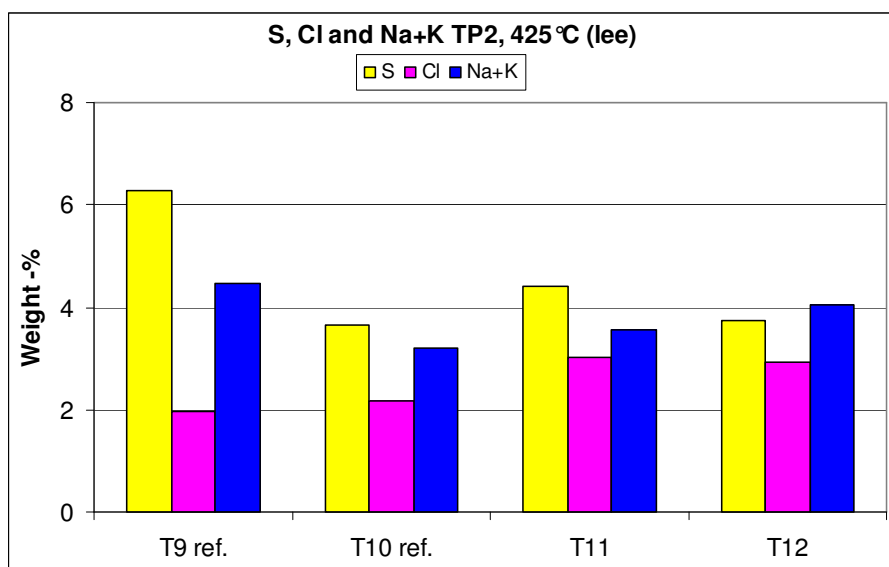
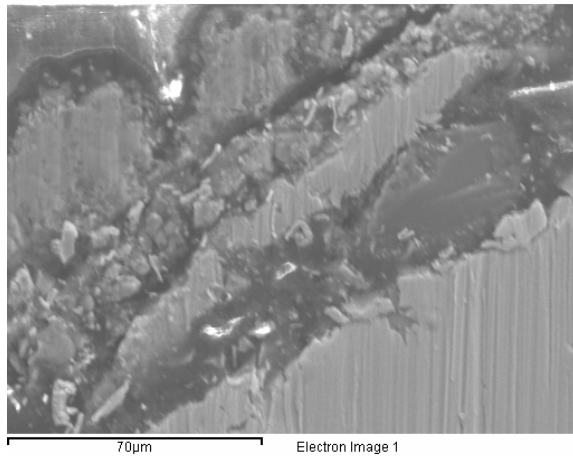


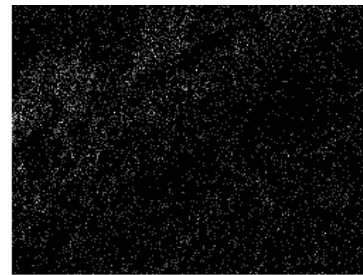
Figure 28, Sulphur, Chlorine and sodium+ potassium in deposits on lee side of deposit rings used during 6-hour tests, Bergkamen

## **Appendix 4**

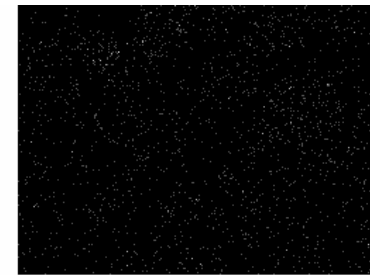
In Appendix 4 are the complete cross-sectional analyses of the rings evaluated in chapter 4.2.5 and 4.3.5 in the report gathered. The carbon (C) analysed is epoxy from the enclosure of the ring that have displaced the loose deposits. Elements above and under the carbon are in reality in connection with each other. The carbon is mostly seen on rings from the 6-hour tests as these deposits were looser and had partly already let go of the ring before the enclosure.



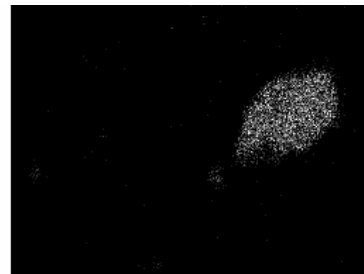
C Ka1\_2



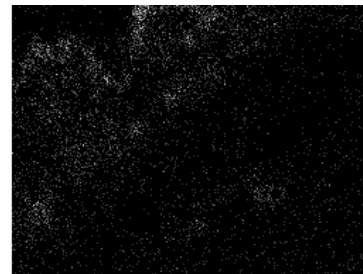
O Ka1



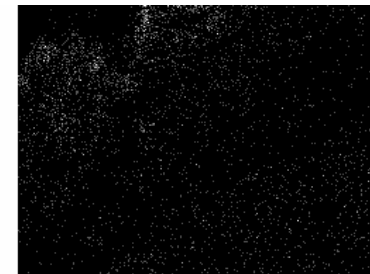
Al Ka1



Si Ka1



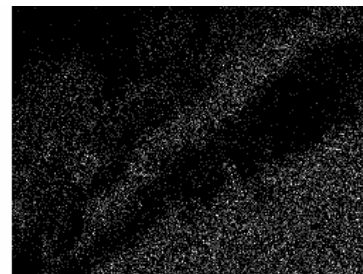
Cl Ka1



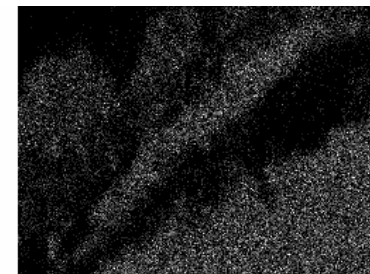
K Ka1



Ca Ka1



Cr Ka1

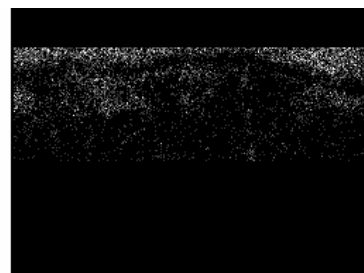
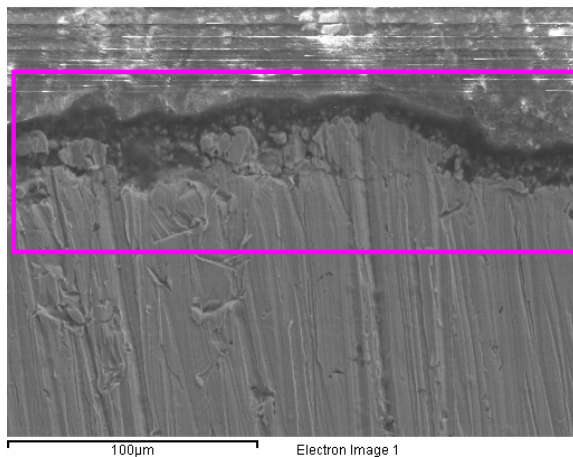


Fe Ka1

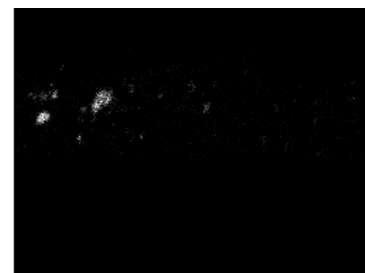


Ni Ka1

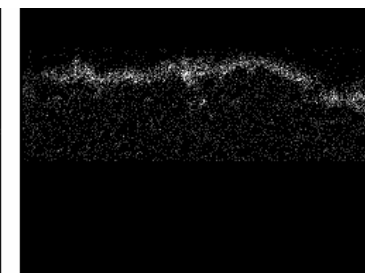
Ring 14 wind from test T5 ref (425°C)



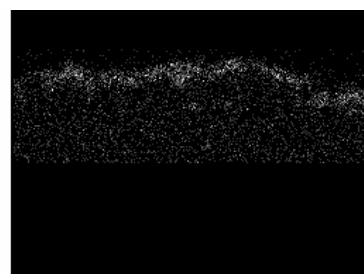
C Ka1\_2



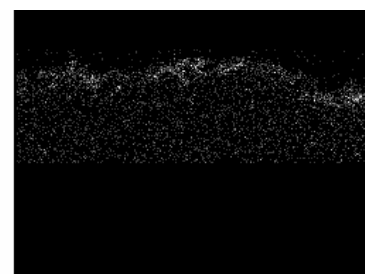
Si Ka1



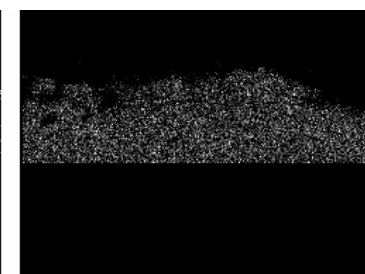
S Ka1



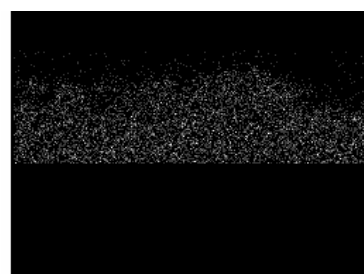
K Ka1



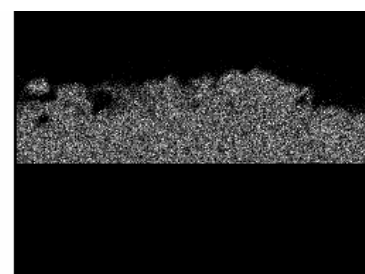
Ca Ka1



Cr Ka1



Mn Ka1



Fe Ka1



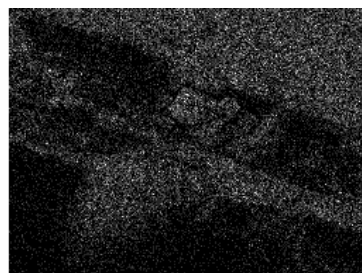
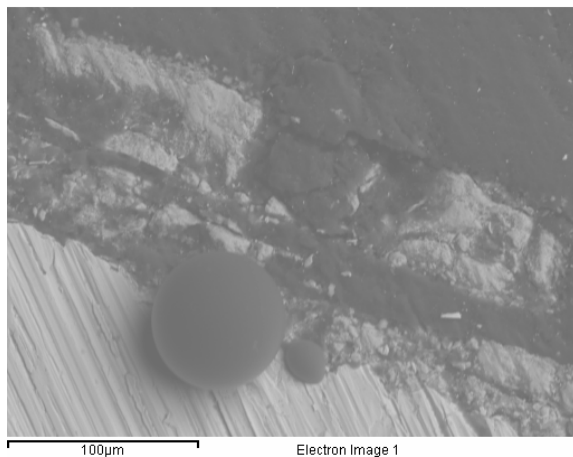
Ni Ka1



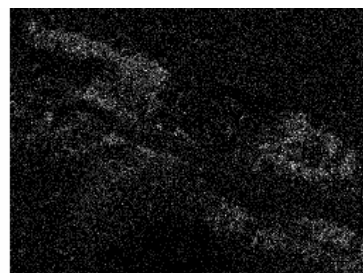
Cl Ka1

Ring 17 wind from test T6 (425°C)

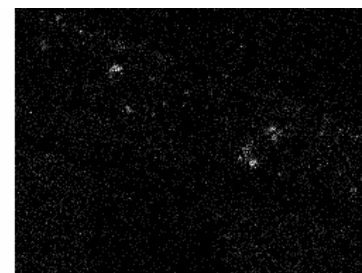




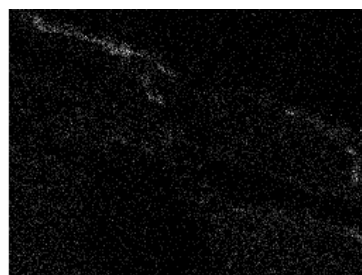
C Ka1\_2



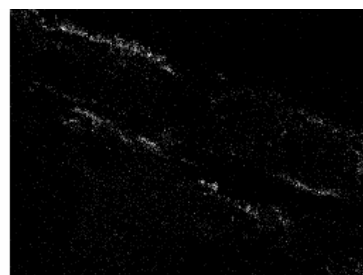
O Ka1



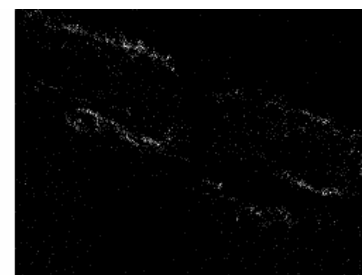
Si Ka1



S Ka1

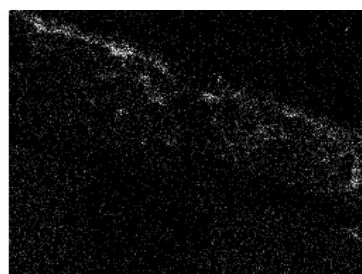


Cl Ka1



K Ka1

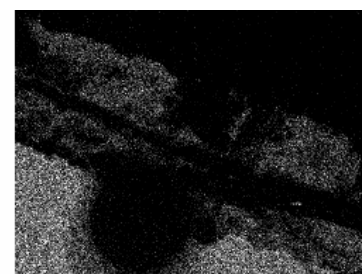
Ring 63 wind from test T10 ref. (425°C)



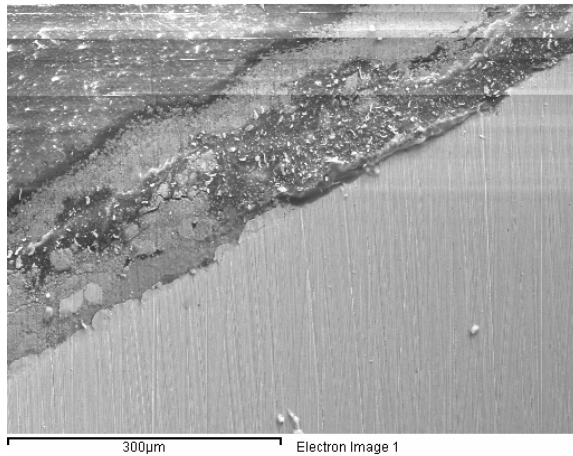
Ca Ka1



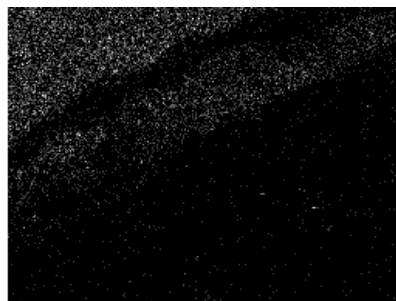
Cr Ka1



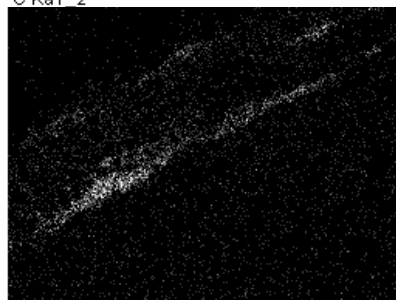
Fe Ka1



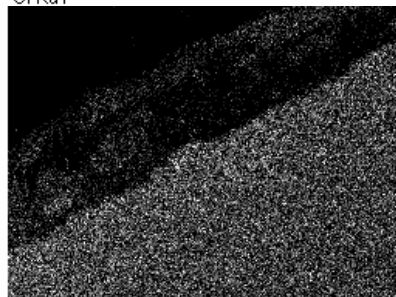
Ring 66 wind from test T11 (425°C)



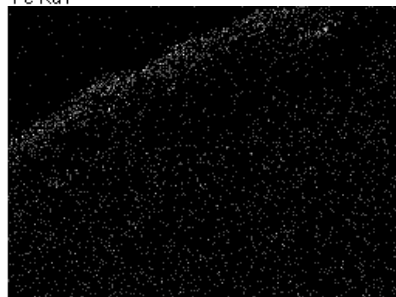
C Ka1 2



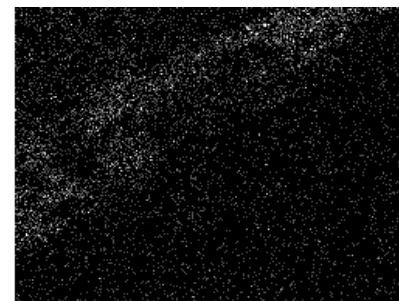
Cl Ka1



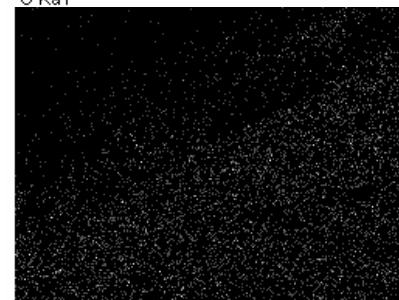
Fe Ka1



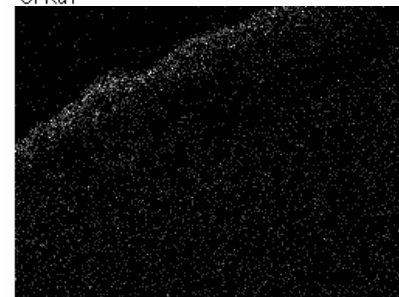
K Ka1



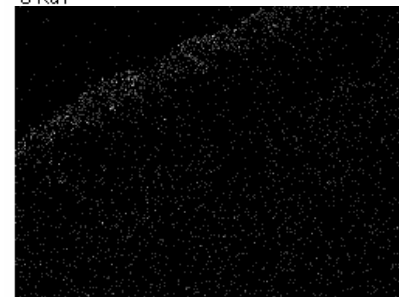
O Ka1



Cr Ka1



S Ka1



Ca Ka1



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